The Principles

of

Physical Metallurgy

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PREFACE TO THE SECOND EDITION

The approach of this text to the subject physical metallurgy has remained in the second edition as it was in the first, namely, that of the classical physics and chemistry. We were determined upon this choice because of the reception accorded the first edition.

More adequate explanations of metallic behavior have recently become available, based upon atomic structure and upon the kinetics of metallic transformations. These have both clarified our understanding of metallic behavior and related metallurgy more closely to the fundamental concepts of present-day science. Recrystallization, creep and fatigue, austenite transformation, age hardening, welding, and powder metallurgy are among the more practical aspects whose treatments in this book have benefited from recent advances.

We are indebted again to a number of reviewers and collaborators, including Dr. E. C. Bain, Dr. H. J. French, Dr. Samuel L. Hoyt, Profs. J. H. Frye, Jr., V. O. Homerberg, M. A. Hunter, C. M. Mason, C. H. Mathewson, R. F. Mehl, J. F. Oesterle, Mortimer F. Sayre, Donald F. Smith, J. C. Slater, and Curtis L. Wilson.

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PREFACE TO THE FIRST EDITION

In 1933 the author collaborated with Donald M. Liddell in the writing of "The Principles of Metallurgy." The demand for a separate text in physical metallurgy is responsible for the appearance of a portion of that book as a separate volume. The opportunity has been taken to rearrange the earlier work, especially to separate it into appropriate chapters; to add a fuller treatment of the subjects of corrosion, heat treatment, and rate of attainment of equilibrium in alloys, and to add also a chapter on the commercial alloys.

The book attempts to supply a unified account of the present-day knowledge of metals and alloys. As in other fields of science, so, of course, in physical metallurgy, even the most basic concepts must constantly be modified as experiment continues. But periodically the account must be summarized. Only thus can a broad perspective be preserved to those working in the field.

The approach to the subject is that of the classical physics and chemistry, beginning with the states of aggregation. As the metallurgists of today begin to appreciate more generally the applicability of physicochemical principles to metallic problems, a new impetus is given to metallurgical research.

It is the principles of metallic behavior which are considered most important in this work, not the individual alloys or processes, however important these may be industrially. For example, the constitution of steel and its heat treatment are discussed in several parts of the book, because steel, as a very important example, is selected to illustrate the principles of constitution and of heat treatment in general. These scattered references for each metal are summarized in Chap. XII.

It is important, however, for the student to know what the commercial alloys are and to learn the basic processes and problems involved in their use so that he may see clearly how these processes and problems are related to the fundamental principles. The ability to recognize the principle which is involved in a problem or, as it is commonly put, the ability to apply principle to

practice, is as necessary to the engineer as is the knowledge of principle itself. Separate consideration of the commercial aspects of the principal metals and alloys is given briefly in Chap. XII.

While it is thus desirable to give some brief notice to the industrial alloys in the same text that discusses the fundamental principles, nevertheless, when the student or engineer reaches a point in his career where he wishes to concern himself in detail with alloys of one type—the steels or the brasses or the aluminum alloys, for instance—he will turn to a separate book devoted to those alloys. A number of such books are suggested at appropriate places in the text.

Part I, The Physics of Metals, together with Chaps. IX and XI on the shaping and testing of metals, can be comprehended before Part II, Metallography, is taken up, so that when used for beginning students, the book thus divides itself naturally into two parts.

The author is indebted to many colleagues and their works, but principally to Professor F. Sauerwald and his excellent treatise "Lehrbuch der Metallkunde," to Professor G. Tammann's book of the same title; to his former teacher, Professor W. Guertler; to Professor C. H. Mathewson for extensive suggestions incorporated in Chaps. I and III; to Dr. John Johnston, Dr. H. W. Gillett, Dr. R. F. Mehl, and many others for valuable criticism and suggestions, and to Professor Bradley Stoughton for unfailing counsel and advice.

GILBERT E. DOAN.

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THE PRINCIPLES
OF
PHYSICAL METALLURGY

INTRODUCTION

The Field of Physical Metallurgy.—Whereas a dozen technical men may be engaged in operating a group of iron blast furnaces or a copper smelting plant in order to extract the metals from the ores and to purify them for use, a hundred men may be engaged in fabricating the metals which have been extracted, forming them into countless shapes, such as rails, I-beams, boiler plate, automobile sheet, brass tubing, copper wires, and iron castings; and a thousand men may be concerned with the working up of these shapes into metallic products for use by the consumer. The automobile plants, the builders of railroad equipment, bridges, and aircraft, the manufacturers of electrical machines and appliances with their heat-treating, stamping, machining, welding, riveting, and plating processes will serve as examples of the final stages in the adaptation of metals to man's use. Therefore, while the processes of extraction of metals from their ores, *i.e.*, the field called *extractive metallurgy*, is of fundamental importance in the metal economy of the country and in the quality of metal obtainable, relatively few individuals will come into direct contact with this older field. In the metal fabricating and manufacturing industries, on the contrary, a large number of persons is engaged. A correspondingly large number of individuals will be interested in the behavior of the metals under the influence of the operations which are there performed upon them. This region of metallurgy is now commonly called *physical metallurgy* (German, *Metallkunde*), although other designations, such as *the science of metals* and *metallics*,[1] are used. It is with this field of metallurgy that this book is concerned.

[1] In consonance with *physics, mathematics, ballistics,* etc.

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Mankind and Metals.—Metals are the physical sinews of modern civilization. If one realizes for a moment that all our tools and machines from the sewing needle and the table knife up to the most powerful engines and machines, our automobiles, our railways, ocean steamers and aircraft, our docks and cranes, our huge skyscrapers and our modern chemical apparatus, and finally everything in which the use of electricity is involved, including the telegraph, telephone and radio, our electric lighting, power transmission, and even power generation, depend upon the use of metallic materials of construction, he has some conception of the part that metals play in our present age.

The complexity of the combination of physical, mechanical, and chemical properties that is demanded of a given metal for a particular use is rather striking, as is also the quantity of metal that is used for each purpose, and its economic value.

It is the task of the metal industry to deliver to the engineering world the raw material and finished products that it demands.

Evolution in Metallurgy.—But the whole of metallurgical practice is in a state of flux and development. The problem is not to maintain present standards but constantly to develop newer and better ones. Many technical problems in the generation or utilization of power, in electrotechnology, in air transportation, and in the chemical industries have been solved from the engineering angle up to the point of obtaining a metallic material with the necessary properties demanded by the new service. Every development in metallurgy releases new possibilities in industry at large. A great deal depends upon the quality and quantity that the metal industry is able to deliver, how well the most suitable metal is chosen for each purpose, how it is treated and improved; in other words, how the metal problems are met.

This control of material is possible only on a basis of the most exact scientific knowledge of the metals, *i.e.*, upon scientific metallurgy. This *science* of metallurgy is only gradually developing out of the *art* of metallurgy of the past. In the end, science will liberate metallurgy from the waste of time and money that always attends empirical methods. It teaches us first what properties we may expect from metallic materials and spares us the search for impossible results. It tells us in general where and how the attainable results are to be sought and thus serves the

metallurgist in a way similar to that in which geology and petrology serve the prospector. It reveals the relation between composition and treatment of alloys and their resulting properties and thus makes possible a successful management of the entire development. Finally it leads to methods for the production of steel and other alloys that are uniform in quality.

These are the services of metallurgy and these its tasks.

In each use a combination of a number of special properties is demanded of the metal; for example, endurance to repeated stresses, elasticity, electrical resistance, specific gravity, and resistance to certain acids. When we consider the complexity of the demands we understand at once why thousands of different alloys are now in use and are necessary, and that with the rapid development of technology the number must constantly increase. Ceaselessly the properties of the alloys are modified by changes in the proportions of these constituents and by new additions. The realization of this situation has led Mr. Tom Mercer Girdler, president of the Republic Steel Company, to state that the steel industry has entered a period of "tailor-made steel."[1] A clear understanding of the principles underlying the countless alloys now in use and a comprehensive understanding of the general principles involved in their superior properties are therefore necessary as a basis for their further development.

In attempting to supply this understanding, the present text sets out to explain the basic nature of metallic substances and their properties in general rather than to describe certain metals and alloys that today are found in most common use. It is the conviction of the authors that in an industrial world, where change is the continuous order of the day, it is more important to develop a way of thinking about metals, a way of understanding their behavior, in short, a "philosophy of metals," than it ever can be to memorize any information, of temporary interest, about individual metals and alloys.

The following chapters attempt to supply that basis.

The Metals.—The combination of properties that the metals possess, and by virtue of which they derive their preeminence for mechanical and structural uses, is essentially the combination of strength *with* plasticity. In addition, they are of course excellent conductors of electricity and fairly resistant to corrosion.

[1] Address before American Society for Metals, October, 1934.

Many brittle substances, glass for instance, have high tensile strengths, as high as 400,000 lb. per square inch, but they lack plasticity under sudden shock. Glass, tar, sealing wax, and—in the earth under tremendous pressures and during millions of years—even rocks flow slowly. But metals may be deformed rapidly by sudden shocks, as in stamping and forging, without fracture. A bridge made of glass might have ample strength, but if not perfectly aligned it would break, whereas a metal bridge could conform to a considerable change of alignment by both elastic and plastic deformation without rupture, in fact without loss of strength.

Whence do the metals derive this peculiar nature? What are the seat and source of these properties? we ask. Are not the metals simply chemical elements in the list of 92 in the periodic table? In what intrinsic ways, then, do the 50 or more metallic elements differ from the nonmetallic elements and from the intermediate "metalloids"? In addition to strength and plasticity, they exhibit a "metallic" luster, are quite high in specific gravity, and feel cold to the touch because of their good conductivity for heat. Whence arise these peculiar properties?

In metallic *compounds*, such as oxides or sulphates, for instance, the metallic atoms are present also, but true metallic properties do not appear. Hence we conclude that these properties are not due alone to the metallic atoms per se but also to a certain arrangement or grouping with respect to each other which these atoms assume when free to do so. In a similar way the bricks and boards of which a house is built determine to only a limited extent what the character of the house will be. Let us examine these two phases of the question separately—the metallic atoms themselves and the grouping or arrangement of these atoms in the "metallic" state.

The Periodic Table.—The most convenient survey of the metallic elements themselves is found in the periodic table, and this convenience is further increased by separating the columns into A and B groups, as is done in Table I. In the usual form of the table, we find in the first column (valence = 1) Li, Na, K, Cu, Rb, Ag, Cs, Au. Clearly, the separation of the elements copper, silver, and gold into a IB group, and of the remaining (alkali) metals into a I_A group, would result in two subgroups each containing metals of quite similar properties. This separation

NON-METALS

Inert gases

TABLE 1. PERIODIC SYSTEM OF THE ELEMENTS

Transition elements

High-melting heavy metals

Low-melting heavy metals

Non-metals

IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA (Fe)	VIIIA (Co)	VIIIA (Ni)	IB	IIB	IIIB	IVB	VB	VIB	VIIB	VIIIB
1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.02	5 B 10.82	6 C 12.01											7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.997	12 Mg 24.32	13 Al 26.97	14 Si 28.06											15 P 30.98	16 S 32.06	17 Cl 35.457	18 A 39.944
19 K 39.096	20 Ca 40.08	21 Sc 45.10	22 Ti 47.90	23 V 50.95	24 Cr 52.01 (α)	25 Mn 54.93	26 Fe 55.85 (α)	27 Co 58.94 (β)	28 Ni 58.69	29 Cu 63.57	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.7
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Cb 92.91	42 Mo 95.95	43 Ma	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7	47 Ag 107.88	48 Cd 112.41	49 In 114.76	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.92	54 Xe 131.3
55 Cs 132.91	56 Ba 137.36	57 La 138.92	72 Hf 178.6	73 Ta 180.88	74 W 183.92	75 Re 186.31	76 Os 190.2	77 Ir 193.1	78 Pt 195.23	79 Au 197.2	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 209.0	84 Po	85? 212 (?)	86 Rn 222.0
87? 223 (?)	88 Ra 226.05	89 Ac 227	90 Th 232.12	91 Pa 231	92 U 238.07												

Rare earths:

57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Il 146 (?)	62 Sm 150.43	63 Eu 152.0	64 Gd 156.9	65 Tb 159.2	66 Dy 162.46	67 Ho 163.5	68 Er 167.2	69 Tm 169.4	70 Yb 173.04	71 Lu 174.99

Strong electropositive metals

Light metals

The numbers in front of the chemical symbols represent the atomic numbers; those following, the atomic weighs. The geometric figures indicate the crystal structure at room temperature.

□ = Face-centered cubic   ▣ = Body-centered cubic   ◉ = One-face centered orthorhombic   □* = Complex cubic   ⬡ = Hexagon   ◇ = Rhombohedral   ⬡(·) = Face centered orthorhombic   ▣ = Body-centered tetragonal   ⬚ = Diamond lattice   ◇ = Monoclinic   α, β = Modification

has, therefore, been made in each of the eight groups as shown in Table I.   With this regrouping into *A* and *B* sections, the metals fall into four or five natural families with close resemblances among the members.   Thus the "light metals," "ductile, high-melting heavy metals," "low-melting heavy metals," etc., will be found to denote groups of metals that resemble each other closely in density, melting point, strength, affinity for oxygen, and other properties.

This classification of the metals into groups enables one to anticipate, merely by knowing to what family it belongs, the properties of a metal with which he is not familiar.   Thus beryllium would be expected to have properties similar to those of its neighbor magnesium, and this turns out to be a well-supported expectation.   Ruthenium would be expected to resemble the five other platinum metals, of which platinum alone is commonly used.   It is thus possible, by familiarizing oneself with the properties of one or two members of a family, to feel fairly sure what properties will be possessed by any other member of the family.

While the resemblances within each family are marked, still, as in the human family, the individual differences between the metals are also quite pronounced, so that if zinc is not suitable in a single respect for a plating to resist corrosion, it becomes most expedient to try another metal lying near it in the table—cadmium, for instance.   Or, again, if vanadium added to steel does not produce the desired result, perhaps chromium, its neighbor, will do so.   Molybdenum may be substituted for tungsten in incandescent lamps, titanium for aluminum in nitriding steels, etc.   So in synthetic and substitutive problems, as well as in general knowledge of the metals, this grouping is of distinct advantage and usefulness.

Metals and Nonmetals.—This grouping does not, however, supply a sharp distinction between metals and nonmetals.   One criterion in this matter is the electrolytic behavior of the elements. This criterion classifies as a metal any element which upon electrolysis of its compounds appears at the cathode, whereas the nonmetals, such as chlorine and oxygen, go to the anode.   Such a distinction serves nicely in the case of copper, iron, and most other metals, but it also includes hydrogen and certain radicals, which

even when solidified do not seem to exhibit strongly marked metallic properties.

Another classification is based on the number of electrons in the outer orbit of the atom. It is found that metallic atoms in the gaseous state do not combine to form polyatomic molecules, such as O_2 formed by oxygen. This is explained by the fact that two metallic atoms, even if they share the electrons in their outer orbits, will not possess enough to complete a stable configuration or shell, as postulated by the Bohr theory of the atom. Thus, aluminum has three *valence* electrons and needing eight for a stable shell it cannot, with only six shared electrons, form a stable diatomic molecule. Aluminum is a metal. Phosphorus, on the other hand, with five valence electrons can easily form a stable shell of eight electrons by sharing three electrons with another phosphorus atom in a diatomic molecule. Phosphorus is a nonmetal. Carbon and silicon each having four and sharing four are just able to form diatoms and in their properties are on the border line between metals and nonmetals, being brittle, low in conductivity, etc.

While these two criteria make it possible to classify certain elements as metals, they do not supply an explanation for the peculiar properties of the metals pointed out at the beginning of this Introduction. An explanation will be attempted again at the end of the first chapter after a preliminary acquaintance with metallic structure has been established.

PART I
THE PHYSICS OF METALS

CHAPTER I

THE STATES OF AGGREGATION

Metallic Vapors.—Vapor-density measurements, as made by Victor Meyer and others, show metallic vapors to be monatomic gases. Metallic vapors should, therefore, and do, obey the gas laws of Boyle, Gay-Lussac, and van der Waals as nearly as other gases do. They thus conform to the well-known kinetic theory of gases. They are quite transparent, as are other gases. Monatomicity is, therefore, the principal distinction of the metals from the nonmetals in the vapor state.

Vapor-to-liquid Transition.—When a metallic vapor is condensed to a liquid, either by an increase in pressure upon the vapor, or by a lowering of its temperature, or both, the kinetic energy of flight of the atoms is so reduced from that which obtained in the gaseous state that the mutual interattractive forces of the atoms for each other (a/v^2 in van der Waals equation), now predominate over their extensive flight. The atoms are brought closer together or "condensed." The random to-and-fro rebound of atoms in the gaseous state is replaced by a more limited amplitude of vibration, or mean free path, as is illustrated by the Brownian motion in liquids containing fine dispersoids. The difference in energy content of atoms in the liquid state and in the gaseous state is called the *latent heat of vaporization* or of *condensation*. The former term is usually expressed in calories of heat required to vaporize 1 g. of the liquid at the boiling point.

The transition from vapor to liquid state (condensation) and vice versa (evaporation) is an important one. Condensation of a vapor may be produced, in general, either by increase in pressure or by decrease in temperature of the vapor.[1] In a closed vessel

[1] The LeChatelier-Braun principle: If a change occurs in one of the factors determining a condition of equilibrium, the equilibrium shifts in such a way as to tend to annul the effect of the change. Thus an increase in pressure shifts the above equilibrium liquid-solid in such a way as to tend to annul the expansion accompanying melting. It shifts the equilibrium liquid-solid to a higher temperature, *i.e.*, it raises the melting point.

containing a pure liquid, molecules (mon- or polyatomic ones) near the surface of the liquid and of higher energy content than their neighbors may escape into the space above the liquid. Here they are little attracted by the highly dispersed vapor molecules and exist as free gaseous molecules. Likewise vapor molecules may impinge on the surface of the liquid and condense. At any given temperature, a dynamic equilibrium between the molecules entering and those leaving the liquid will exist. The pressure of the vapor molecules against the walls of the closed container at any given temperature is called the *vapor pressure* of the liquid at that temperature. The vapor pressures of some pure metals are given in Fig. 1. The change of pressure
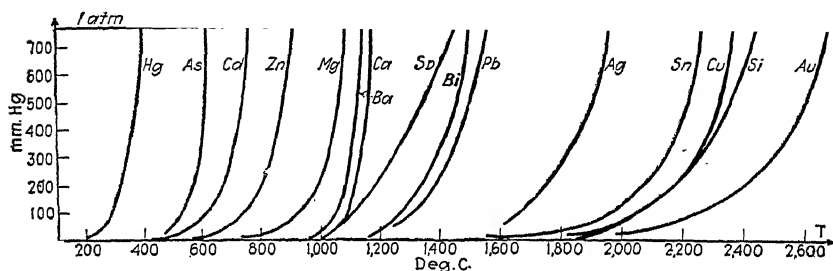
FIG. 1.—Vapor pressures of pure metals.   (*Guertler-Leitgebel.*)

with change of temperature may be given by the Clapeyron-Clausius equation $dp/dT = \lambda/T\Delta v$, where λ equals the latent heat of vaporization of the substance and Δv is the change in volume.

Critical Conditions.—If the pressure in the closed vessel is increased, the temperature remaining constant, it will result in disappearance of the vapor phase,[1] since the two phases can coexist in equilibrium at any temperature, only if the corresponding pressure obtains. (Gibbs's phase rule for a one-component system.) If the temperature of the system is raised and the pressure is allowed to increase naturally with rise in temperature, then the liquid, being less susceptible to pressure, expands owing to temperature rise; and the vapor, being more susceptible to pressure, becomes denser owing to compression. At a certain temperature and pressure the vapor is so dense and the liquid so rarefied that the two states are indistinguishable. This con-

[1] As illustrated in Figs. 2, 3, and 4.

dition is called the *critical condition,* and the corresponding temperature and pressure, the *critical temperature and pressure.*[1]

The PVT Diagram.—These relationships are best illustrated in the diagram of Fig. 2 for the system ice-water-water vapor. The line *ad* represents the specific volume of the liquid and the line *cd* of the vapor as the temperature and pressure are raised by heating in a closed vessel. The point *d* is the critical point. *a*
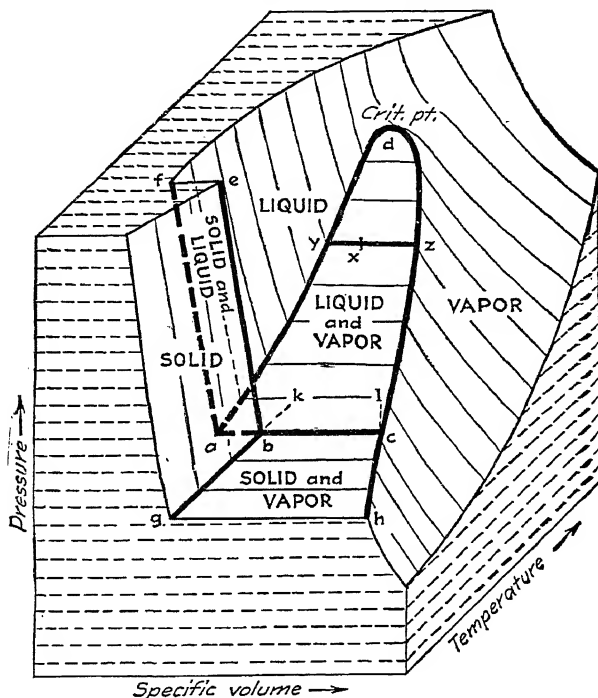

FIG. 2.—Constitutional diagram for the system ice-water-water vapor. (*Rivett.*)

represents the specific volume of the liquid and *c* (to a shortened scale) that of the vapor, *b* that of ice (greater than that of the liquid because water expands upon freezing whereas most metals contract) at the one temperature and pressure at which all three phases can coexist.

If the pressure is increased at this constant temperature of the triple point (for this system +0.0076°C.), the vapor disappears[2]

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[1] See footnote on p. 11.

[2] This is true only when ice, water, and water vapor exist alone without contamination of O_2, N_2, etc.

and we enter the field marked "solid and liquid." The volumes of both solid and liquid diminish as shown by the slope of the lines *be* and *af*. If the temperature is lowered from +0.0076°C., at constant pressure, the liquid disappears to form more ice and we enter the field marked "solid and vapor."

If the diagram of Fig. 2 is projected, for simplicity's sake, upon the temperature-pressure plane, it will appear as in Fig. 3, which will be familiar to all students of physical chemistry. Most metals contract on freezing instead of expanding as water does, so the line *AE* for most metals slopes to the right and upward as the pressure rises, instead of to the left as in this figure for water.
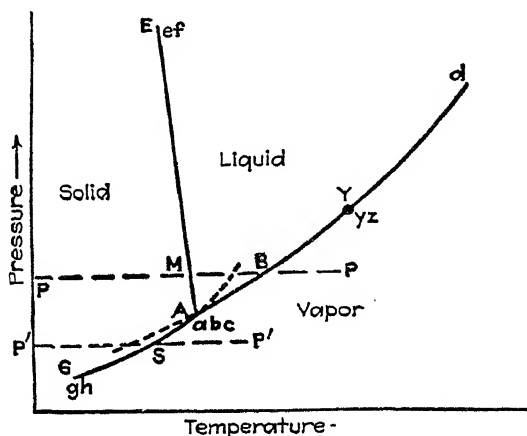
Fig. 3.—Temperature-pressure diagram for ice-water-water vapor. (*Rivett.*)

For a typical metal the *PT* diagram would appear as in Fig. 4, where the *melting point* and *boiling point* (the temperature at which the vapor pressure is 760 mm.) are 232 and 2250°C., respectively. The effect of increase in pressure is to raise the melting point slowly (LeChatelier's principle), and the boiling point rapidly, due to the greater increase in volume upon vaporization as compared with the increase upon melting.[1] Lowering the pressure reduces both points and they may meet as at *T*. This point is called a *triple point* (the projection upon the *P-T* plane of the line *ac* in the three-dimensional diagram of Fig. 2). Here three phases—vapor, liquid, and solid—coexist. If this point happens to lie above atmospheric pressure for a certain substance, instead of below atmospheric pressure as in Fig. 4,

[1] See footnote on p. 11.

heating that substance causes not melting but *sublimation*, as in the heating of iodine or of solid CO_2 (dry ice). (If heated under a bell jar, the pressure of the CO_2 vapor formed finally results in a high enough pressure to cause melting as is illustrated in Fig. 4.)

Some General Properties of Liquids.—Two properties of liquids are especially important in metallurgical operations, such, for instance, as casting liquid metals into molds: they are *viscosity* and *surface tension*. The specific heat and the solubility for gases are important also and are considered in Chap. III. Viscosity is internal friction resulting in a resistance of the liquid to flow. It may be conceived as the rubbing and interference of molecules flowing past each other during motion of a liquid. Thus molecules of dumbbell shape would produce a higher viscosity than would spherical ones. Viscosity is measured in liquids,

Fig. 4.—Temperature-pressure diagram (schematic) for the conditions of tin.

such as lubricating oils, in seconds of time required for a given weight of liquid to flow through a given orifice, under a given gravitational head, and at a certain temperature. Its reciprocal

Fig. 5.—Surface tension of liquid metal preventing sharp castings.

is called *fluidity*. In casting liquid metal into a mold with long canals or recesses, it is necessary for the metal to reach and fill the extremities of such recesses before solidification. Hence the viscosity must be low, *i.e.*, the rate of flow must be rapid. Otherwise the metal will not fill out the mold and the casting will be incomplete.

Surface tension, another property of liquid metals of importance in casting, is the force that causes the surface of a liquid, when free, to assume a spherical shape, as a rain drop or a globule of mercury. If sharp castings, as in printer's type or in screw

threads, are desired, this spherical tendency may result in rounded instead of sharp edges, as shown in Fig. 5. To avoid this condition, castings may be made under a pressure sufficient to overcome surface tension and to force the metal into sharp edges, as in pressure die casting; or minute additions to the metal may be made to lower its natural surface tension. For this reason antimony is useful in type metal, improving the sharpness of the letter faces.

Surface tension may be conceived as originating in the forces of Newtonian attraction between the molecules in the liquid. In the interior of the liquid each atom is surrounded closely by similar atoms and is in dynamic equilibrium under the attractive forces of all its neighbors. At the surface of the liquid the exterior "half" of each atom or molecule is in contact with air or a vapor, the atoms of which are highly dispersed and able to exert a correspondingly lesser attraction for the surface molecules of the liquid. These surface molecules are, therefore, drawn inward and laterally toward each other more strongly than outward, and in this condition act as a dense, tightly drawn skin over the surface of the liquid. (Surface tension is measured as the force in dynes necessary to separate an element of this surface layer 1 cm. long.) *Capillarity, i.e.,* the rise (or depression) of liquids in narrow tubes, is an evidence of surface tension.

Surface tension diminishes with rise in temperature and becomes zero at the critical temperature (where the vapor and liquid states are indistinguishable). The surface tensions of metals are usually high compared with those of other liquids. The surface tension of water is about 25 and of alcohol about 72 dynes per centimeter at room temperature. That of aluminum is about 500 and of iron about 1,500.

Differentiation between these two properties of liquids—fluidity or rate of flow, and surface tension or extent of flow—is made easy by consideration of a familiar substance, molasses. Its fluidity is low, so that if "cast" into a mold at low temperature it would freeze before it has flowed very far. But even at the lowest temperature at which it is liquid it would fill sharply those crevices which it reached before freezing, since the surface tension is comparatively low. Mercury, on the contrary, has quite high fluidity but also a relatively high surface tension.

Liquid-to-solid Transition.—The solid or, as we shall see more correctly, the "crystalline" state in metals is by far the most important in engineering construction. And yet it would not be clearly understood without a knowledge of the vapor and the liquid state.

Continued abstraction of heat and lowering of the temperature of a liquid result in a continued decrease in the extent and rapidity of vibration of the molecules of the liquid until at a cer-
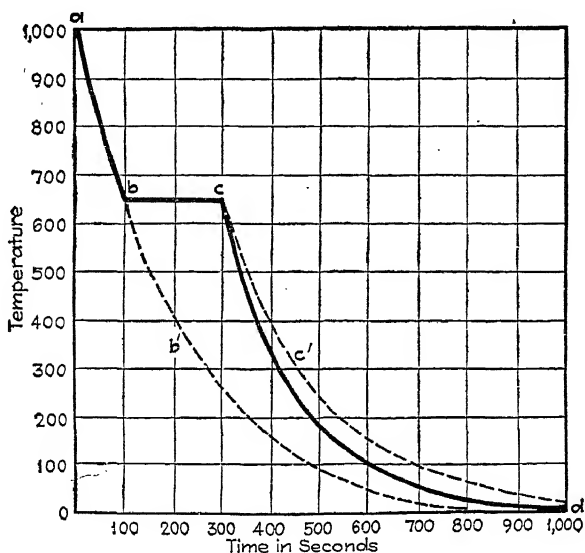

FIG. 6.—Simplified time-temperature graph showing freezing of a pure metal. (*Ruer.*)

tain temperature, known as the *freezing point*, the molecules "fall" into relatively fixed positions with respect to each other. These positions might perhaps better be called *centers of oscillation*, for, although the random to-and-fro motion of molecules characterizing the vapor and liquid states has disappeared, still, all motion of the molecules has by no means ceased after solidification. It is merely reduced to oscillation about a fixed point. The difference in energy content of the liquid and solid states is known as the *latent heat of fusion*. It is usually expressed in calories of heat required to melt 1 g. of the solid at the melting temperature. The cooling curve of a pure metal is shown in Fig. 6.

The evolution of this latent heat at the freezing point causes a halt in the gradual drop in temperature of the body that is cooling. A uniformly cooled melt would follow the line *ab b'* of Fig. 6. At *b* evolution of the latent heat begins, and the temperature cannot fall farther until all such heat ceases to be liberated, *i.e.*, until crystallization is complete. From point *c* downward the course of the curve would be *cc'* if it were not that the specific heat of the solid is almost always *less* than that of the liquid. As a result, the curve follows *cd* instead. Similar considerations hold for polymorphic transformations.

Frequently the liquid will drop far below its true freezing point before crystals become visible. The phenomenon is called *supercooling*. A familiar example is the supercooling of pure water in an undisturbed beaker several degrees below 0°C., its true freezing point.

The Atom and Its Importance.—Before considering further the physics of metals, it is necessary to have a usable concept of the internal structure of the atom, for the atom is the building stone of matter, and the properties of matter in all three states of aggregation may be explained in terms of internal structure. The picture of the atom as presented by Rutherford and Bohr and developed by later workers represents the atom as being composed of electrons, protons and neutrons. The protons constitute the positive charge of the atom and together with the neutrons are concentrated at the center of the atom, constituting most of its weight. The electrons balance the protons in charge, and are most simply represented as being arranged in concentric shells about the nucleus. When these shells contain a definite number of electrons, they are stable, *i.e.*, they have no tendency to take on or give up any electrons. Proceeding outward from the nucleus, the number of electrons per stable shell, as designated in the periodic table, is 2, 8, 8, 18, 18, 32, and 6. For any element the number of electrons associated with the nucleus is equal to its atomic number. Thus with sodium, which has an atomic number of 11, there are 11 electrons associated with the nucleus, and arranged in shells of 2, 8, and 1. The one electron in the outer shell is known as the *valence* electron.

The electrons in the atom are in motion in the space around the nucleus, and are also spinning on their own axes. A crude analogy may be drawn between the electron traveling in its orbit

around the nucleus and spinning on its own axis, and the earth
traveling in its orbit around the sun and spinning on its own axis.

Each shell of electrons around the nucleus constitutes a definite
energy band.   These bands are labeled from the nucleus out-
ward, the first band or shell being the K band, the second the L
band, etc.   The inner or K band has the lowest energy, the outer
band the highest energy.   In 1925 Pauli, a physicist, put forth
his mathematical principle, which states that each band is
divided into one or more energy levels, and further, that not more
than two electrons can exist in any given energy level at the same
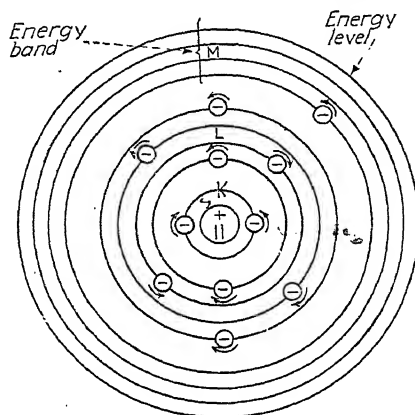
Fig. 7.—Na atom, one half of the first M level and all three higher levels are unoccupied.

time.   Each electron will spin in an opposite direction.   Con-
sequently, each energy band must be subdivided into sufficient
energy levels to accommodate all the electrons in that band, two
to a level.   Figure 7 presents a schematic arrangement for the
element Na.

Having once established this theoretical electronic configura-
tion, modern physics demands that we no longer consider the
electrons as finite particles, but as wave motions.   For conven-
ience, however, we may consider the concentration of these waves
into points as being analogous to the Bohr electron.

As we shall see later, it is the valence electrons located in the
outer band of unfilled energy levels, and free to migrate accord-
ing to Pauli's theory under external excitation, which largely
account for metallic properties.   Table III gives the electronic
arrangement of free metallic atoms as accepted today.

The Atoms in a Crystal.—The positions of the atoms in the crystalline state form definite unit patterns, which are called *space-lattice* units. (More accurately these positions should be

Cubic	Hexagonal	Tetragonal
(a)	(b)	(c)
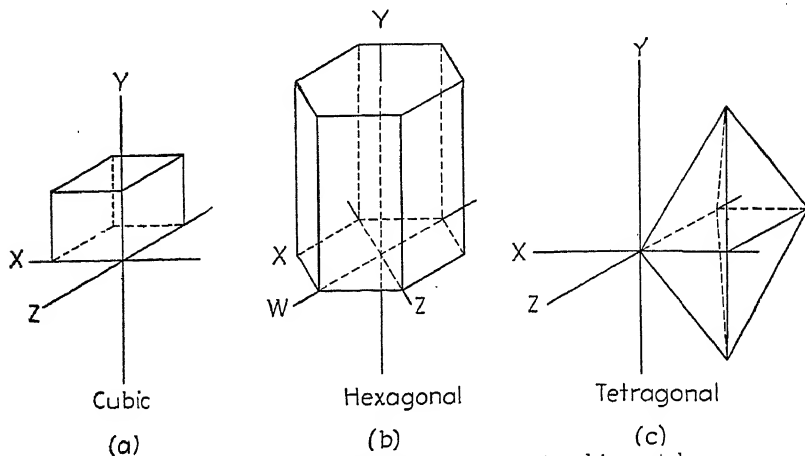
. 8.—Common crystal systems encountered in metals.
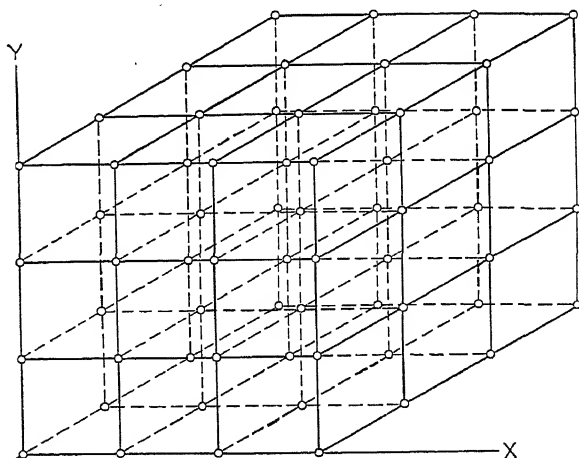
Fig. 9.—Space lattice built up from simple cubic unit cells of type shown in Fig. 8a.

called *centers of oscillation,* for they are in motion.)   Fortunately, only three different patterns, and these of the simplest type, are encountered in the most important metals and they can be

handled easily on the basis of elementary geometric relationships. Consider the three simple geometric systems—the cubic system, the hexagonal system, and the tetragonal system—shown diagrammatically in Fig. 8*a*, *b*, and *c*.

Body centered cubic

Face centered cubic

(a)   (b)
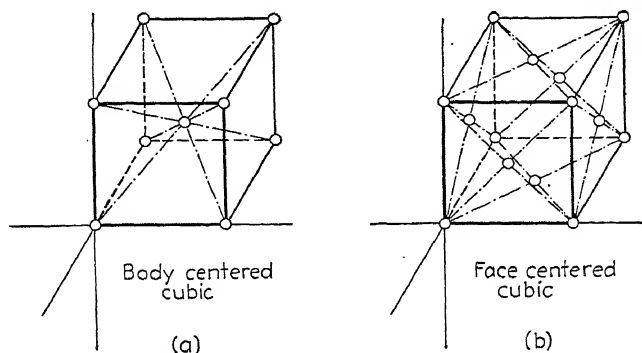
Fig. 10.—Modifications of the simple cubic system encountered in metals.

If each of the corners of these units is assumed to represent the center of the atom, or more correctly its sphere of influence, then these corners represent the positions of the atoms in a crystal
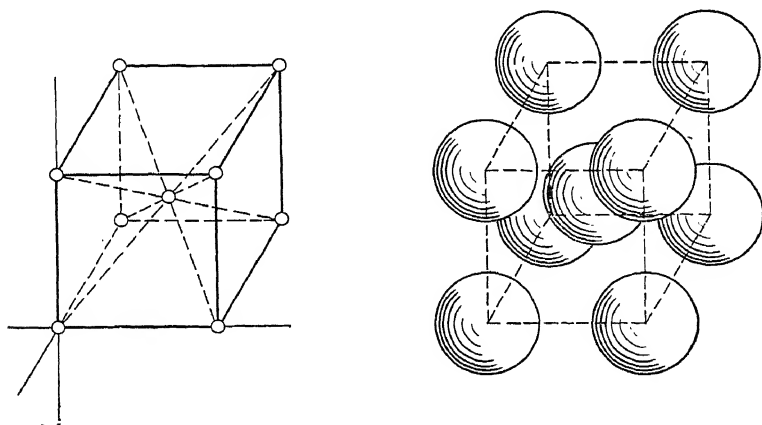
Fig. 11.—Body-centered cubic system. Common body centered metals, Cr, V, Mo, W, Na, K, Mn, and αFe.

relative to each other. They may conveniently be referred to an arbitrarily chosen set of axes. The unit cells or space-lattice units may be likened to the bricks of which the crystal is built, for they are grouped together continuously in sufficient numbers

to make up the volume of the crystal as illustrated in Fig. 9 for the simple cubic system.

No metal actually crystallizes in the simple cubic pattern as indicated by Fig. 8*a*, but many do in either of two modifications
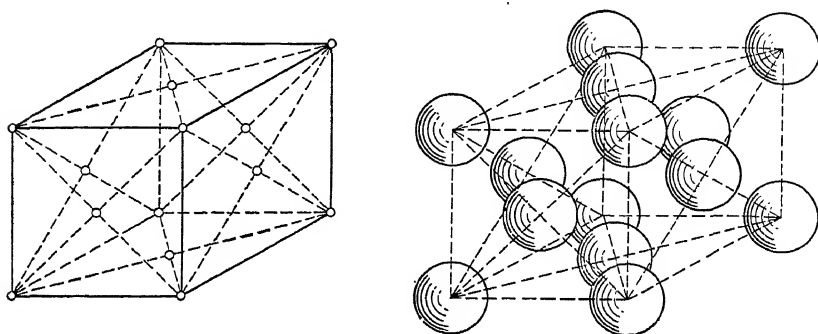
Fɪɢ. 12.—Face-centered cubic system.   Common face-centered cubic metals; Al, Cu, Ag, Au, Pt, Pb, βCo, βNi, and γF

of that pattern.   The body-centered cubic system places an extra atom at the center of each unit cube, and the face-centered cubic system places an extra atom in the center of each of the six
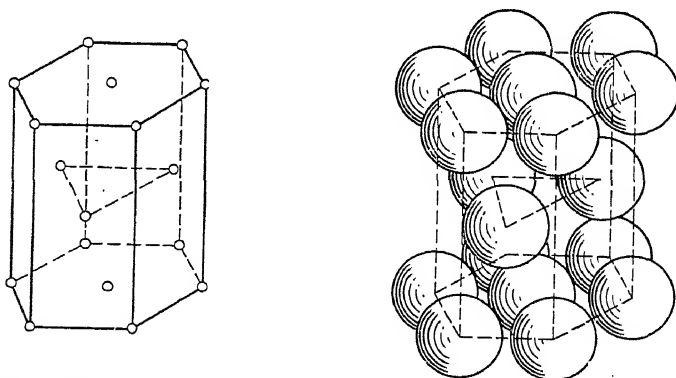
·Fɪɢ. 13.—Close-packed hexagonal system.   Common close-packed hexagonal metals, Mg, Zn, Cd, αCo, αNi.

cube faces.   These modifications of the cubic system are pictured in Fig. 10*a* and *b*.

Considering the spheres of influence of the atoms to be represented as actual spheres, the unit cells are pictured in Figs. 11, 12, and 13.

In our present state of knowledge, the reason for a given metal's solidifying in any one of the three systems is unknown. However, it is known that each metal tends toward the condition of lowest potential energy, and the lowest energy of electrostatic attraction between the atoms. Those metals that solidify in the face-centered cubic system or the close-packed hexagonal system actually attain that condition which is the closest packing of spheres. Such packing may be exemplified by the piling of cannon balls. If a first layer of spheres is laid down as closely as possible, the appearance will be shown by the full circles in Fig. 14, revealing equilateral triangles connecting the centers

X = Position of atom centers in third layer in hexagonal close packed arrangement

O = Position of atom centers in third layer in face-centered cubic arrangement
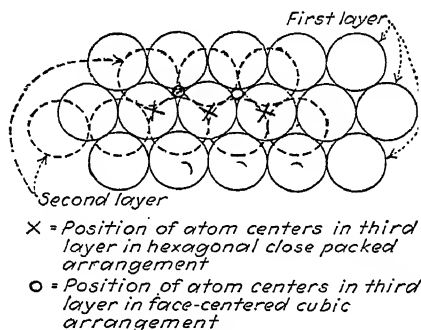
FIG. 14.—The piling of spheres to represent the positions of atoms in a crystal.

of each three spheres, or a centered hexagon of seven spheres. In placing the second layer on top of this one, each sphere (dotted) lies in a hollow between three spheres which form a triangle in the first layer. But it should be noticed that only every alternate triangle in the first layer can be so loaded. The third layer can be laid down in either of two ways. (1) Each sphere (x indicates its center) may be laid vertically over a sphere in the first layer. This method of packing results in the hexagonal close-packed arrangement. (2) Each sphere (marked with a smaller circle) in the third layer may be laid over the centers of the triangles in the first layer, which were skipped in laying the second layer. This arrangement is the face-centered cubic arrangement.

It should be noted that when the unit cells are incorporated into the space lattice (Fig. 9), the eight corner atoms of the unit cube belong equally to eight neighboring cubes, so that only one-eighth of the eight corner atoms belongs to each unit cell,

making one atom per unit cell. The body-centered cubic arrangement adds one more atom per cell, making two atoms per cell.

The condition of orderly internal arrangement of the crystal is the essential condition of the crystalline state. Although we are accustomed to think of crystals as bodies with regular symmetrical boundary planes, we now realize that external symmetry is merely an evidence of something more fundamental, namely, regular arrangement of atoms within the crystal. Faces on a crystal and planes within a crystal are always sheets of atoms, and all edges on a crystal and directions within a crystal are lines of atoms. The physical and chemical characteristics,
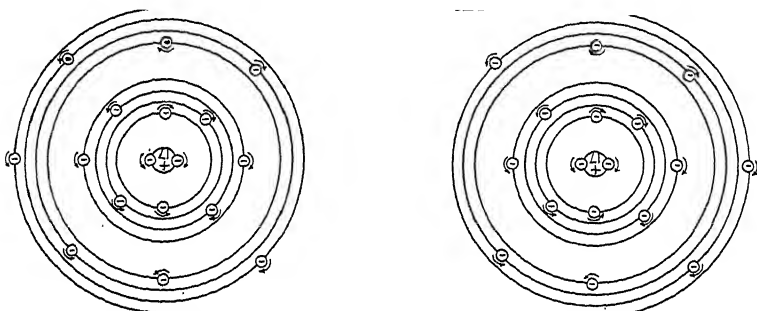
15.—Schematic illustration of the covalent bond in a Cl_2 molecule.

such as the coefficient of expansion, conductivity, solubility, and strength, are determined not only by the composition of the substance, but also by the arrangement of the particles, *i.e.*, by the space lattice.

The Metallic Bond (Lattice Energetics).—If, as has just been seen, the metallic crystal is built up of a regular arrangement of a large number of neutral atoms, what holds those atoms together? That is an altogether legitimate question because it has forced the physicists to recognize a new type of atomic bond, *i.e.*, the metallic bond.

In crystals of the NaCl or ionic type, the force of attraction is primarily of a simple electrostatic nature between Na^+ ions and Cl^- ions. The metallic crystal obviously cannot contain ionic bonds, since all the atoms constituting the crystal have the same positive valence.

In other cases of the nonmetallic type, the binding forces are primarily of a covalent nature in which neighboring atoms share

valence electrons in order to build up stable electron shells. For example, two Cl atoms with a valence of −1 share one of their seven electrons in their outer shells with each other, thus building up a stable external shell and forming a Cl_2 molecule. Figure 15 illustrates this type of bond. It can be shown that a pure covalent bond in the case of metals would be unstable.

The lack of oppositely charged ions in the metallic lattice and the lack of sufficient valence electrons to form a stable covalent bond thus necessitate the sharing of the valence
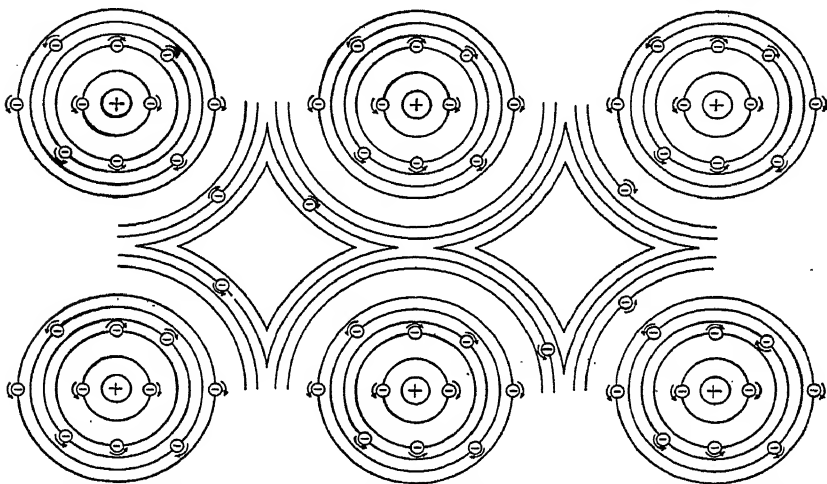
FIG. 16.—Schematic arrangement of an Na crystal showing the sharing of valence electrons.

electrons by more than two atoms if the stability of the metal crystal is to be understood. The sharing of valence electrons in an Na crystal is illustrated schematically in Fig. 16. We must thus conceive of the cohesive forces in a metal crystal as belonging to a large electronic system, composed of a "negative gas" of electrons, free to move among the + metallic ions in definite energy levels, and holding together the + metallic ions by virtue of their mutual attraction for that negative gas. This point of view is in keeping with our fundamental concept of the atom and with Pauli's principle. As we shall see, this concept will also make possible the interpretation of metallic properties.

√ **Crystals vs. Liquids.**—It is important at this point to note the fundamental difference in the crystalline state with its closely ordered, regular arrangement of atoms, as compared

with the vapor and liquid states and their utterly random, disordered state of aggregation. The attractive force between the atoms in the crystalline state is higher than it is in either the liquid or the vapor state, because the atoms are so much closer together (except bismuth and antimony). It is not surprising, then, to find that crystals are harder and stronger than either liquids or vapors.

On the basis of this distinctive character of the crystalline state, as contrasted with the liquid and vapor states, Tammann has proposed to abolish the old classification of matter into solid, liquid, and vapor states and to substitute the classification crystalline—noncrystalline. As we shall see, there is good support for this proposal. It is at once apparent that between the crystalline and liquid states there can be no critical point at which the two states become indistinguishable, as is the case between the liquid and vapor states described above (for the atoms will either be in the space-lattice positions or out of them). Glass, being noncrystalline, would be classed with liquids and vapors.

Some General Properties of Crystals. Anisotropy.—In the vapor and liquid states, the properties, such as conductivity of electricity and heat or diffraction of light, are the same in whatever direction through the substance the measurements of these properties are made. Substances in these states have properties that are scalar but not vectorial and are said to be *isotropic*. In the crystalline state, with its geometric arrangement of atoms, it is not surprising to find that these properties vary if the direction in which they are measured through the crystal varies. For instance, if a property is measured in a direction through the crystal *parallel* to the layers of atoms, it will be different from the measurements made at an angle to these layers. Thus crystals of graphite conduct the electric current one hundred times better in one direction than in a direction at right angles to the first direction. The modulus of elasticity of an Armco iron crystal is 13,500 kg. per square millimeter in the [100] direction and 29,000 kg. per square millimeter in the [111] direction. Because of this vectorial character, crystals are said to be *anisotropic*. The rate of solution in acids also differs in different directions of the crystal. Etch pits, characteristic of each crystal form, arise in this way on the surface of a metal immersed in a corrosive medium.

Crystal Surfaces.—Each atom in the interior of a simple cubic lattice is surrounded by six equidistant atoms, each located a distance equal to half the diagonal of the cube, from the center. Every atom is in this same relative position to its neighbors and is in equilibrium under the action of all these six forces.

The exposed electronic gas at the surface of a crystal may be conceived of as grasping gaseous atoms, resulting in the *adsorption* of gases on metal surfaces, and accounting for the strange effects of metal surfaces, as of platinum in the *catalysis* of chemical reactions. If the size of the crystal is greatly reduced, an increasing proportion of the atoms will be at the surface and these surface effects become predominant. This is the condition known as *colloidal dispersion*. Colloidal particles are crystals containing from 1,000 to about 1,000,000 atoms.

Crystal Imperfection, Mosaics.—The structure of crystals, thus far in our studies, has been assumed to be geometrically perfect. However, the work of Darwin has shown conclusively that, in order to account for certain peculiarities in the intensity of X-ray reflection, crystals must be fragmented internally. These fragments seem to form a mosaic of small blocks inclined to each other at a small angle so that there is a slight interruption of the regular crystalline pattern at the boundaries of these fragments. The exact nature of this mosaic is not known, but indications are that it is at least statistically regular. Just as the mosaic is necessary to explain the variation in intensity of X-ray reflections, so is a similar form of imperfection necessary to explain the observed strength of crystals. The strengths of crystals, calculated on the basis of the strength of the atomic bond and the number of such bonds in the cross section, are from 100 to 1,000 times greater than those actually obtained. A. Griffith, at the Second International Congress for Applied Mechanics, at Delft in 1924, showed mathematically that small notches or imperfections within glass rods acted to concentrate the applied stress to such an extent that locally the strength of the atomic bonds was exceeded and that failure proceeded progressively from those notches and at a very low total stress.

The explanation by Griffith inspired a more detailed investigation of crystal perfection from both the theoretical and the experimental point of view. Perhaps the most active investigators in this field have been Smekal, Orowan, Zwicky, Joffe,

G. I. Taylor, and M. J. Buerger. The results of these men, although differing in detail, show that the crystal lattice is not perfect, but is interrupted by minute flaws due to the mechanism of crystal growth.

These imperfections, when they occur at the surface, are most dangerous, as is shown mathematically by Orowan and demonstrated experimentally by Joffe. Joffe has found that a crystal of NaCl, when fractured in air, has a tensile strength of 0.5 kg. per square millimeter, while the calculated strength was 200 kg. per square millimeter. When immersed in hot water, the NaCl crystal was found to have a strength of 160 kg. per square millimeter, which compares favorably with the calculated value. The water seems to have healed the surface imperfections. Smekal, on the basis of a "secondary structure" of imperfections, has pointed out that the properties of crystals may be divided into two classes. (1) The *structure insensitive* properties are such as density, specific heat, compressibility, coefficient of expansion, and lattice structure. These properties are practically the same for single crystals and polycrystalline samples of the same substance, they change very little on cold working and annealing, and they are not greatly affected by the introduction of small amounts of impurities. (2) The *structure sensitive* properties are such as the mechanical and electrical breakdown strength of crystals, the hysteresis losses accompanying mechanical vibrations, the work hardening of metals, and the ferromagnetic phenomena. These latter properties may differ in different samples even when no difference can be detected by chemical analysis, or by X-ray or microscopic examination. Smekal attributes these structure sensitive properties very largely to his "secondary structure."

Polymorphy.—Variation in temperature or pressure of a crystal, without melting or vaporization, may cause it to change its crystal structure, *i.e.*, the form of its internal arrangement of atoms. The ability of a material to exist in more than one crystalline form is called *polymorphy*. Thus, heating to 907°C. causes iron to change from body-centered cubic (α) iron to the face-centered cubic (γ) form. These polymorphic changes are influenced by changes in pressure at constant temperature just as are the changes in melting and boiling that we have considered above. A complete temperature-pressure diagram for a crystal

showing these polymorphic transformations is given in Fig. 4. Just as, for instance, in melting, if the change in crystalline state is accompanied by expansion, a rise in pressure will raise also the temperature at which the transformation occurs (principle of Le Chatelier and Braun). The properties of one polymorphic form of the same metal will differ from those of another form. For example, γ iron can dissolve up to 1.7 per cent of carbon, whereas α iron can dissolve only 0.03 per cent.

Summary.—The crystalline state, we now see, is characterized by an orderly arrangement of positive metallic ions in a space lattice. These ions are held together by their mutual attraction for a "gas" of (negative) valence electrons which is shared among them. These arrangements may change without the melting of the metal. Such changes are called polymorphic. The lattice arrangements for most metals are simple ones and are most frequently in the cubic system. Regular internal arrangement, not external form, is the essence of crystallinity. The properties of crystals vary with the direction of measurement through the crystal.

With this preliminary knowledge of the crystalline state of aggregation, we are now prepared to examine more closely the mechanism by which this state originates from such preexisting states as the vapor or the liquid.

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THE ORIGIN OF METALLIC STRUCTURE

Origin by the Freezing of a Liquid.—If liquid metal, for example, that in a crucible, is allowed to cool slowly and, after it is cold, if the solidified metal is sectioned, polished, and etched by a chemical reagent, and examined, usually under the microscope, the appearance is that of a regulus of metallic grains (see Fig. 17). Tammann has pointed out that this structure originates in the following way.

When the melted metal in the crucible or mold has dropped slightly below its melting point (slight supercooling), *nuclei* of the crystalline phase appear spontaneously at points in various parts of the liquid. The atoms that first start to form crystals probably are those in the lowest energy states of the Maxwellian distribution. If the liquid metal were transparent and the nuclei large enough to be visible, the appearance would be somewhat as shown in Fig. 18a. At each of these points adjacent atoms begin to "join hands" with each other, giving up at this instant their energy of liquid motion as latent heat of fusion at the boundary of the growing crystal and adopting, instead of their random motion, relatively stationary positions with respect to each other, thus forming a crystal lattice. The atoms are not motionless in the lattice, at temperatures above absolute zero, but oscillate about the points indicated. If the observer were inside one of these growing crystal lattices and looked about him in any direction, he would find a periodic recurrence of atoms in whatever direction he looked throughout the lattice.

The nuclei now grow[1] by the orderly accretion of other atoms from the liquid, and these atoms take up similar positions about

FIG. 17.—Polygonal grain structure in pure tungsten. Oriented luster. (*Jeffries.*)

Nuclei at inception of freezing	Partial solidification; Dendritic cross nuclei	Completion of crystallization Growing crystals meet
(*a*)	(*b*)	(*c*)
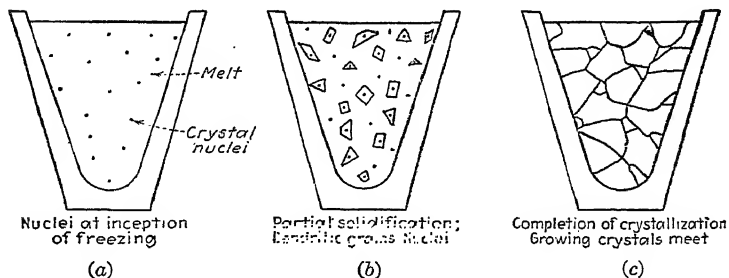
FIG. 18.—Progressive freezing of a uniformly cooled melt.

the nuclei. The appearance at an intermediate state during freezing would be somewhat as shown in Fig. 18*b* or, in case of

[1] During melting, the reverse of crystallizing, it seems that for some metals a few nuclei remain in the melt even after the temperature is above the true melting point. Filtration of melted organic compounds as salol and thymol through hot glass wool seems to remove certain particles. Thereafter these liquids show no tendency to spontaneous crystallization even when cooled far below the melting point (MEYER and PFAFF, *Z. anorg. Chem.*, April 7, 1934).

dendritic growth, as shown in Fig. 19 for NH_4Cl crystals forming in a labile supersaturated solution. During growth, other "crops" of nuclei are, of course, constantly springing up in the

FIG. 19.—Dendritic crystals of NH_4Cl growing in a supersaturated solution. (*Tutton.*)

liquid. The number of nuclei forming per second in a unit volume of liquid at a certain temperature is called the *rate of nucleus formation* at that temperature (N). The rate at which
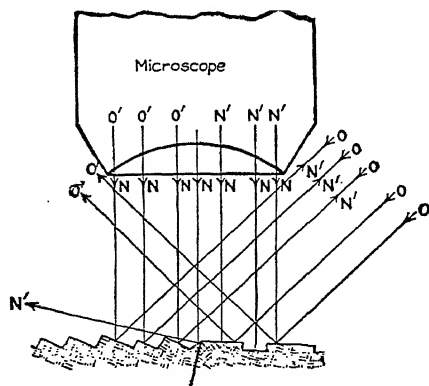
FIG. 20.—Origin of light and dark appearance of grains in pure tungsten of Fig. 14. (*Rosenhain.*)

these crystal nuclei grow at any given temperature is called their *rate of crystal growth* (G).

Finally, the growth of each crystal is mutually obstructed by that of its neighbors and with this obstruction comes exhaustion of the liquid between the crystals.. Solidification is complete as

shown in Fig. 18c. The final boundaries of the "crystals" are not symmetrical but are compromises between the abutting "crystals." They are, therefore, called not crystals but *crystallites* or *crystalline grains*, or simply *grains*. Since the orientation of the nuclei usually depends on chance, the orientation of the grains in the final object is random. This random orientation results in the unequal reflection of light from the grains after etching, causing some to appear darker than others in Fig. 17. This condition is illustrated both for normal and for oblique illumination in Fig. 20. Those grains that reflect light not into
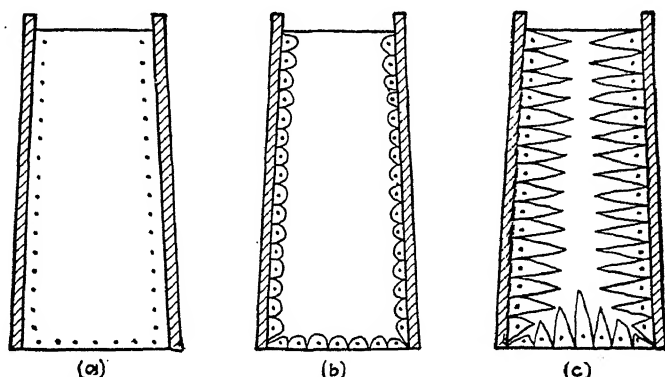
FIG. 21.—Crystal formation in a chill mold (schematic).

the eyepiece but outside it will appear dark. The oblique rays "O" (oblique illumination) make those grains appear light which in vertical illumination appear dark, and vice versa.

A Test Case. Chill Casting.—The theory of crystallization given above explains adequately the final structure of *equiaxial grains* (equal diameters in all directions) shown in Fig. 17. To test it, let us apply it to a condition of abnormal solidification and see whether it retains its validity. If a melt of steel is poured into a relatively cold metal mold, as an ingot mold, the metal nearest the walls of the mold will be the first to drop below the freezing point. Numerous nuclei should thus form near the walls of the mold and begin to grow in all directions, as shown in Figs. 21a and 21b. Vertical and circumferential growth about each nucleus soon results, however, in mutual obstruction of these crystals by their neighbors, but they are at liberty to grow inward toward the center of the mold as the metal cools. The result

should be long crystals radial or perpendicular to the surface of the mold, as shown in Fig. 21c.   That this condition actually occurs in chilled castings is shown in Fig. 22.   Such elongated

FIG. 22.—Columnar grains perpendicular to cooling surface in a chilled casting.

grains are called *columnar*.   If the mold has sharp edges, a plane of weakness will develop at each edge of the casting, the plane halving the angle as shown in Fig. 23a. This weakness is due to the fact that at this plane both gaseous and solid impurities are concentrated, due to rejection by the growing crystals.   Such ingots may break in rolling or forging.   To avoid this plane, most ingot molds are provided with rounded corners (Fig. 23b).   The theory of growth from nuclei thus seems supported by this abnormal test case.

When the melt cools in a sand mold or in a preheated metal mold where the heat conduction of the mold is lower, the metal at the center of the casting may drop to its crystallization temperature before the columnar grains have invaded the center.   In

(a)   (b)
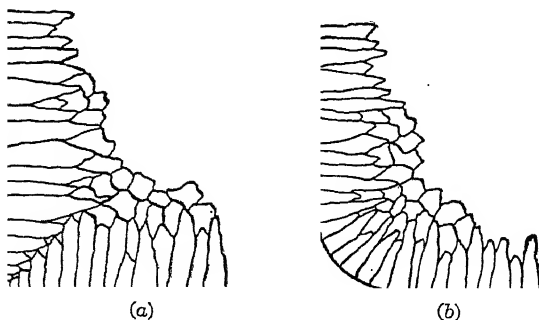
FIG. 23.—(a) Plane of weakness halving the angle in a sharp-cornered mold; (b) elimination by rounding the corner.   (*Desch.*)

this case equiaxial crystals will grow in the central region and the solidified metal will show columnar grains near the surface and equiaxial grains in the interior as in Fig. 22, top center.   The

mold may also be preheated by superheating the melt before pouring.

In chill casting the columnar grains may show not a random but a preferred orientation with respect to the cooling surfaces, *i.e.*, the layers of atoms in each crystallite may have the same angle with respect to the walls of the mold as do those of the other
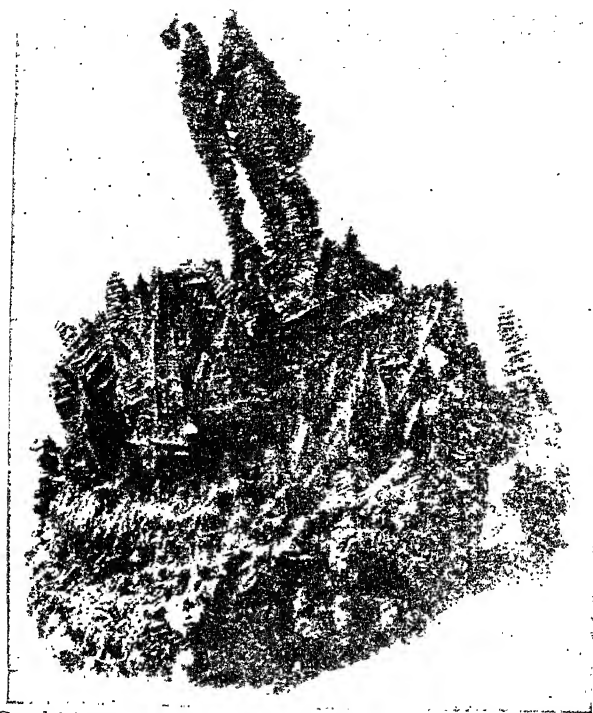
FIG. 24.—Dendritic crystals of iron from the pipe in a cast steel ingot of 0.55 per cent carbon. (*Goerens.*)

crystallites.[1] For example, in the columnar grains of a chilled copper casting a cube face of the lattice of each grain is parallel to the chilling surface (Tammann). The properties of an aggregate of crystallites oriented in a preferential manner, as in a chilled casting, may be called *quasi-anisotropic*.

The Form of the Grains That Grow in a Liquid.—Most metallic crystals withdrawn from the melt show dendritic or pinetreelike

[1] See Fiber Structure, p. 103.

shapes, as shown for steel in Figs. 24 and 25. It has been suggested that the eight corners of a cube immersed in a melted metal would cool more rapidly than the sides of the cube, and growth of the corners would be more rapid, resulting in these dendritic shapes. The orientation of atoms is, however, uniform throughout the dendrite. Sodium chloride crystals grown in a solution containing a colloid, as gum arabic, also exhibit dendritic growth. If the primary dendrites were of different composition from the later layers around them, their presence would be revealed after completion of freezing as in Fig. 26. It should be noted, however, that the crystallites do not generally interlock with each other. In the final stages of solidification the accommodation of one crystal boundary to another prevents them from preserving any regularity of outline. While their exterior boundaries are thus

Fig. 25.—Drawing of an iron dendrite.
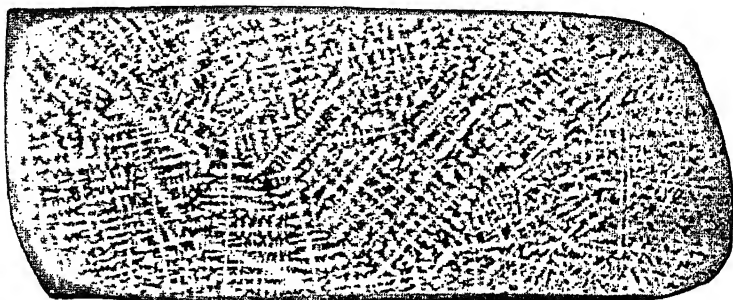
Fig. 26.—Dendrites of nearly pure iron in a steel casting.   (*Sauveur.*)

irregular, their interiors are, however, still perfectly crystalline. The metalloids, such as silicon and antimony, may develop nearly perfect cubic crystals in certain alloys. In other cases the crystal faces may be rounded by the forces of surface tension which, at the temperature of precipitation, may be greater than the crystal's rigidity.

The Size of the Grains in a Casting.—If the *rate of crystalline growth* at a certain temperature below the freezing point is G and the *rate of nucleus formation* is N, then the grain size S of the finished casting will be proportional to these rates, or $S = f\dfrac{G}{N}.$ Since both these rates change with the temperature (degree of supercooling), it is impossible to evaluate the above expression. Most metals, however, exhibit a finer grain size when cooled rapidly (chill cast) than when cooled slowly (sand cast). The three possible conditions are shown diagrammatically in Fig. 27. Both G and N are zero at the melting point, but upon supercooling they increase in value at different rates. For instance, in Case 1 the rate of crystal growth increases faster than the rate of nucleus forma-
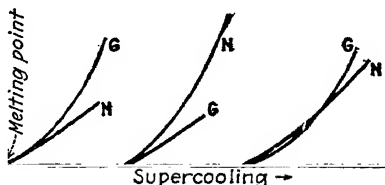
FIG. 27.—Three possible rates of nucleus formation (N) and grain growth (G). (*Goerens.*)

tion. That means that more metal will solidify during freezing by growth of a few crystals than by formation of new nuclei: the grain size will be large. In Case 2 the N-curve lies above the G-curve and the grain size will be small. In Case 3 the curves cross. The structure will contain two regions, one of fine-grain size and one of coarse-grain size. It seems possible to increase N artificially, and therefore to decrease the grain size, in casting aluminum-silicon alloys by the addition of a fraction of a per cent of sodium to the melt. The result is a very fine-grained structure with superior properties, called a *modified structure*.[1] In Fig. 28, both rates G and N are increasing rapidly as the degree of supercooling increases. At lower temperatures, however, G reaches a constant value and at still lower temperature drops nearly to zero, where all atomic mobilities are low. N likewise reaches a maximum, after which it decreases, as shown at 1 in the same figure.

Glass possesses very little tendency to crystallize until it reaches temperatures far below its freezing point, as shown at 2 in Fig. 28, and at these temperatures G is too slow to be effective. Hence, glass rarely crystallizes. Ancient glass does sometimes show crystallization or "devitrification" which has been achieved

[1] See Figs. 278a and 278b.

over a long period.   Metals, unlike glass, cannot be retained in the solidified amorphous state.

Czochralski has shown that if the melt is kept accurately at the melting temperature and the surface touched by a tiny crystal, growth of this crystal will extend downward into the melt.   If it is withdrawn slowly, a single crystal, *i.e.*, a body containing only one orientation of atoms, can be produced. Other methods, such as the use of a slight temperature gradient in a tube, are also used to produce single crystals from a liquid.

Factors Affecting Nucleation.—It has been pointed out that energy is released when the liquid-to-crystalline transition takes place.   This energy decrease is manifested by the liberation
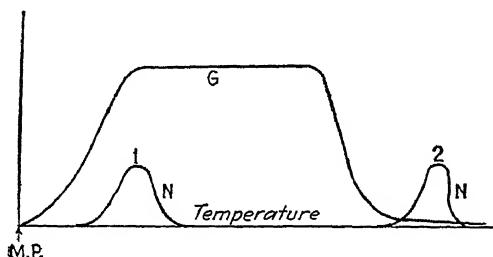
FIG. 28.—Rates of nucleus formation *N* at 1 for metals, at 2 for glass, at various temperatures below freezing.   *G* is the rate of crystal growth.

of the latent heat of fusion.   It has not been noted previously, however, that the creation of a phase interface (*i.e.*, the creation of a solid nucleus in the liquid from which it forms) requires the consumption of energy.

Thus, in order that a stable nucleus may form, the energy supplied in the liquid-to-crystalline transition must at least be equal to the energy consumed in the formation of the new surface.

Small nuclei have a relatively high ratio of surface area to volume (surface area decreases as the square of the diameter, while volume decreases as the cube of the diameter).   Since the total heat liberated depends upon the number of atoms in the nucleus, and therefore upon the volume of the nucleus, the volume must be sufficiently large to supply the energy necessary to maintain its surface.   Thus a minimum size of nucleus is necessary in order that it shall be stable and not redissolve.   Any nucleus smaller than the minimum will redissolve in the liquid even though the liquid is below its freezing point.   Since the

energy liberated upon crystallization increases at lower degrees of supercooling, it follows that smaller nuclei will be stable at these lower temperatures.

It has been pointed out on page 30 that the atoms that form nuclei are those in the lowest energy state of the Maxwellian distribution. The congregation of such atoms in a liquid to form a crystalline nucleus depends upon chance. It is evident that chance will more frequently provide small groups of such atoms than large ones, therefore at low temperatures, where such small nuclei are stable, the rate of nucleation will be a maximum.

Insoluble Impurities in Castings.—It is important to note that any impurities in the melted metal, which are not soluble in the crystals that separate, will usually remain in the liquid phase and will concentrate in the final film of liquid between the crystals. In this position a very small quantity of brittle impurities may form a complete brittle film around each grain and render the entire alloy brittle, as is the case when as little as 0.005 per cent of bismuth is present in copper. The films of iron sulphide around the grains of steel are probably the cause of the hot-shortness of high-sulphur steels. Films of thoria may prevent grain growth in tungsten filaments. Films of oxides are thought to inhibit grain growth in certain steels.

The purest cadmium, even when double distilled in a vacuum, still shows this filmy network as a residue after the cadmium is dissolved out of the network with a 40 per cent ammonium nitrate solution (Tammann). The film consists usually of oxides, silicates, carbides, and sulphides.

The insoluble materials also may freeze before the metal does. For example, the Al_2O_3 formed in the "killing" of an ingot of steel has a melting point far above that of the steel. It solidifies long before the steel begins to freeze. In this case each inclusion may serve as a nucleus for crystal precipitation and appear within the grains rather than at their boundaries, thus promoting a fine grain size. Such inclusions of nonmetallic materials (slag, oxides, refractories, dross) are sometimes called *sonims* (solid nonmetallic inclusions). They appear clearly on the polished, unetched surface of a specimen and can be identified. They weaken the metal. Such metal is sometimes said to be "dirty." Holding the metal liquid for some time before casting permits some of these impurities to rise to the surface, depending in part

on the difference in specific gravity of the inclusions and the liquid metal. Superheating the metal before casting, decreases its viscosity and may aid in the escape of these inclusions. If they are liquid they may coalesce. The larger particles thus formed will offer less surface friction per unit of volume to the liquid through which they rise, and will escape faster.

In this same connection, it is of interest to note in passing that the cohesion between the grains in a normal casting, instead of being weak, actually is stronger, at temperatures far removed from the melting point of the metal, in all but rare instances, than

Fig. 29.—Intercrystalline fracture in bronze. Note the exposed grain surfaces. (*Courtesy of A. M. Bounds.*)

the cohesion within the grains themselves, so that rupture of a metallic object usually takes place *through* the grains and not between them. Such fracture is called *transcrystalline fracture*. An example of the opposite occurrence, *intercrystalline fracture* in bronze, is shown in Fig. 29. Transcrystalline and intercrystalline fracture will be discussed in Chap. III.

Origin by Polymorphic Transformations.—Metallic structure may originate from a preexisting metallic structure. When pure iron freezes, the crystals are formed of atoms in the body-centered cubic arrangement (δ iron). At about 1411°C. the lattices of the δ iron crystals change their form (polymorphic change) to the face-centered cubic (γ) modification. Apparently the origin of this new phase takes place in a manner similar to the formation of the crystalline phase in a liquid; *i.e.*, at points throughout the

existing delta crystallites, usually at the grain boundaries, transformation to the γ lattice begins and gradually spreads until mutual interference of the growing crystals obstructs further growth. The mechanism of the change is not absolutely known, but stages during the change are known. The evidence indicates that it is a gradual and ordered change within the existing lattice. The properties of the object will change gradually (the temperature remaining constant) until all the old phase has disappeared. A degree of supercooling is required in polymorphic transformations, just as it is for nucleus formation in the liquid state. If the rate of cooling is rapid, the grain size after transformation is usually small, for the same reason that chilled castings usually have a fine grain size; that is to say, either the rate of nucleus formation increases or the rate of grain growth decreases as the degree of supercool is increased. If the original grains were encased in thin shells of impurities, it is probable that the new crystallites, however coarse, will not trespass these boundaries, so that with slow cooling the structural appearance after transformation is similar to that immediately subsequent to solidification. At about 900° the Fe crystallites again change their internal dimensions, and this time return to the body-centered cubic arrangement (α iron), with smaller lattice dimensions (than δ iron), corresponding to the lower temperature.

Other metals that are known to exist in more than one crystallographic form are cobalt, cerium, thallium, tin, manganese, and chromium. Tin between 18° and its melting point is in the body-centered tetragonal form (white tin β), and below 18°C. it is in the diamond cubic form (gray tin α) (see Fig. 4). Introduction of the gray variety into contact with the supercooled white tin at temperatures below 18°C. accelerates the transition. Such introduction is called *inoculation*.

Other Modes of Origin of Metallic Structures.—Metallic reguli may be produced also by the condensation of metallic vapors. This has been accomplished in the preparation of very pure zinc and magnesium by distillation. Figure 30 shows columnar crystals of magnesium formed by condensation of magnesium vapor on a cold surface. The growth of crystals from the vapor phase, as the formation of hoar frost, seems to originate in nuclei and to lead to dendrites under similar conditions to those under which they occur in the liquid state. Reguli may be produced

by electrolysis of a metal-bearing solution as in nickel and chromium plating or in the extraction and refining of copper and zinc.

Metallic reguli may also be produced by the compression and heating, or "sintering," of metal powders, as for instance the tungsten[1] powder from reduced tungstic oxide in the preparation of metal lamp filaments, or the formation of the so-called *oilless* bearings from compressed copper and graphite particles; in the
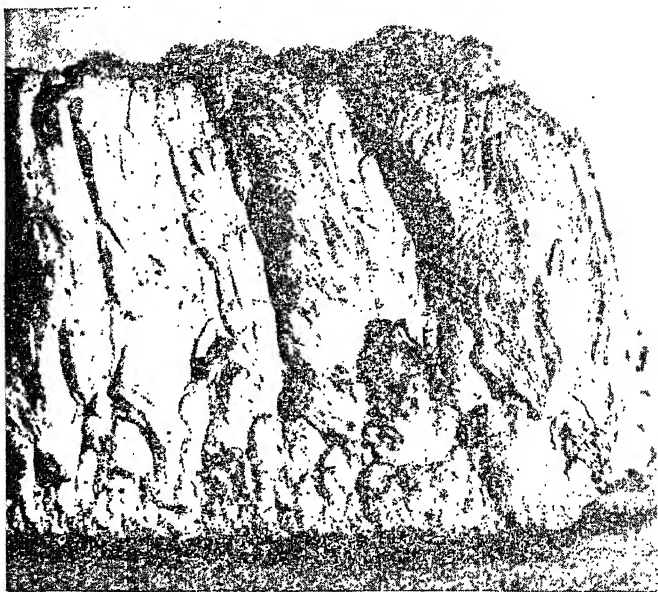
Fig. 30.—Columnar magnesium crystals condensed from the vapor state on a cold surface.

production of Carboloy, which is a sintered tungsten carbide set in cobalt; or Elkonite, which is a sintered spongy mass of tungsten into the capillary pores of which liquid copper has been drawn. The latter material is used for welding dies.   The tungsten retains its stiffness when hot and the copper supplies electrical conductivity.   Evidently grain growth across the boundaries of two adjacent crystals takes place under heat and pressure.[2]   This is the so-called *powder metallurgy* in which the question of particle

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[1] Tungsten melts at some 3400°C., which no common refractory will withstand.

[2] See also Welding, p. 300.

size frequently is important. Powder metallurgy is discussed on pages 284–289.

In electrolytic deposits there seems also to be involved a rate of nucleus formation and of grain growth. When the compound electrolyzed is a simple molecule, the grain size obtained is usually coarse, hence electroplating is usually carried out with complex molecules, such as cyanides, to obtain a fine-grained deposit and a lustrous surface. High-current density produces a finer grain size, yielding however loose metallic powders if a dilute solution is used.

TABLE II.—FIBER STRUCTURE OF ELECTROLYTIC DEPOSITS (*Glocker*)

Element	Electrolyte	Current density, amp. per sq. cm.	Parallel to current flow
Ag	0.1 N AgNO$_3$	0.01	[111] and [001]
Cu	1 N CuSO$_4$	0.03	[011]
Ni	Nickelammonsulphate	0.005	[001]
	0.1 N NiCl$_2$ + 0.9 N NiSO$_4$	0.005	[001]
Ni	0.9 N NiCl$_2$ + 0.1 N NiSO$_4$	0.005	[211]
Ni	—	.....	[011]
Pb	1 N lead perchlorate	.....	[211]
Cr	(Grube)	.....	[111]
Fe	10 % ferroammoniumsulphate	0.001	[111]
Fe	50 % ferrochloride	0.001	[111]
Fe	50 % ferrochloride at 100° + CaCl$_2$	0.1	[112]

Electrolytic deposits may show the crystallites preferring a certain orientation with respect to the direction of current flow. A few of these preferred orientations are given in Table II. The presence of colloids, such as glue or gelatine in the electrolyte usually aids in producing a lustrous surface and a fine grain size, as in electroplating.

Random orientation is obtained at higher current densities for silver from a potassium cyanide solution and for iron. Zinc and cadmium also give random deposits.

The General Properties of Reguli.—We have now seen how the orderly crystalline state emerges from the disorderly liquid and vapor states and from a preexisting crystalline state. We have

seen that the familiar metallic object is composed of an aggregate of crystalline grains of various sizes, the grains being in a more or less random orientation with respect to each other. This random orientation of the multitude of crystals in a metallic object leads naturally to a masking of the vectorial properties of the individual crystals in it, so that measurements of electrical or heat conductivity, for instance, made in different directions through a normal metallic object yield like results. The vectorial properties of the individual crystallites have been averaged, owing to their random orientation in the object.

X RAYS AND CRYSTAL STRUCTURE

The Significance of the Planes in a Crystal Lattice.—It has been of fundamental interest to single out one crystal from a metallic regulus and to study its nature and behavior alone, free from the complicating grain-boundary conditions in the polycrystalline mass. Obviously the behavior of the mass cannot be completely understood without understanding the behavior of the individuals of which it is composed. This field is the study of crystal structure, in which such rapid strides have been made in the last 25 years. Previous to the year 1912, the symmetry of the crystal was one of the "riddles of the ages." Because the solid state of matter did not obey the gas laws and the laws for dilute solutions, it was given very scant consideration by chemist and physicist. The future, therefore, now seems especially bright.

The layers of spheres, described on page 23, may be considered as planes, the nucleus of each sphere in a certain layer lying in the plane which represents that layer. Not only may these planes be passed in horizontal and in vertical directions, so as to contain a number of atom nuclei, but they may be passed in an infinite variety of directions, as shown in Fig. 31 (a section through a crystal lattice). The lines (intersections of lattice planes with the page) of the original lattice are fairly thickly populated with atom nuclei. But the planes 11 are even more thickly populated, while the planes 31 are less thickly populated. It will be noticed that the most densely populated planes are those with the greatest interplanar distance, while the sparsely populated planes lie much closer to each other. It is evident that the planes of sparse atomic population have less physical significance, because the atoms in them are so far apart as to be rela-

tively unaffected by the attractive forces of each other; whereas in the planes of dense atomic population, all the mutual inter-atomic forces of the crystal come strongly into play. Thus the slip planes in a crystal are usually parallel to the planes of dense atomic population and do not cross these planes. We are thus led to the conclusion that only those planes of dense atomic inhabitation (and great interplanar distance) are of important physical significance in the crystal. The other

Fig. 31.—Section through a crystal lattice.

planes are in many cases merely geometrical constructions.
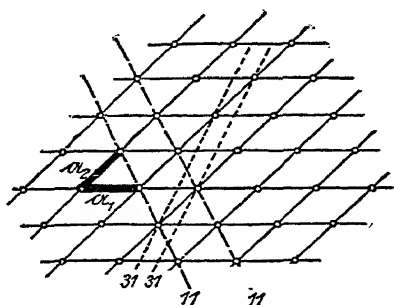
The Location of Planes in a Crystal Lattice.—We have seen that the regular arrangement of atoms throughout the crystal
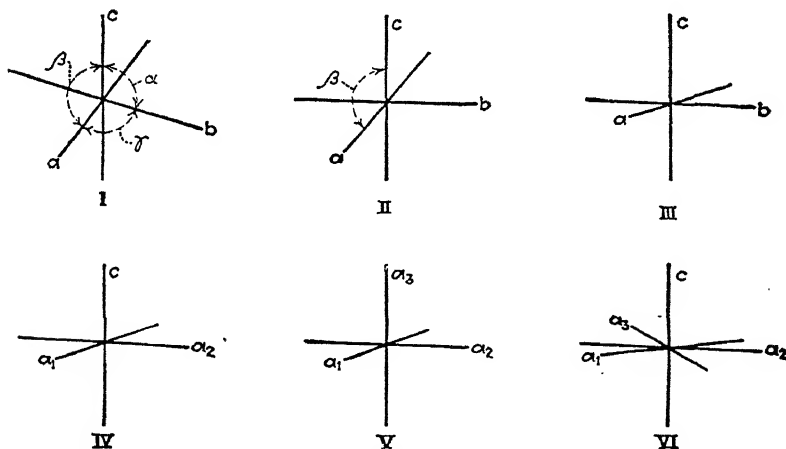
Fig. 32.—Coordinate axes of crystal systems.

I.	Triclinic	$a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90°$
II.	Monoclinic	$a \neq b \neq c,\ \alpha = \gamma = 90°,\ \beta > 90°$
III.	Rhombic	$a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$
IV.	Tetragonal	$a_1 = a_2 \neq c,\ \alpha = \beta = \gamma = 90°$
V.	Cubic	$a_1 = a_2 = a_3,\ \alpha = \beta = \gamma = 90°$
VI.	Hexagonal	$a_1 = a_2 = a_3 \neq c,\ \alpha = \beta = 90°,\ \gamma = 120°$

makes it possible to pass planes in different directions through the crystal, on which planes the atomic nuclei will be more or less densely distributed. The locations of these planes and directions in a crystal are most conveniently described by

them to the coordinate axes of three-dimensional space, shown for the various crystal systems in Fig. 32. A plane is defined by the length of its intercepts on the three axes, measured from the center of coordinates. For simplicity's sake, the *reciprocals* of these intercepts, known as the *Miller* indices, are generally used. Thus, in a simple cubic crystal one of the cube *faces* lies

(100) *(a)*   (110) *(b)*

(112)

(c)
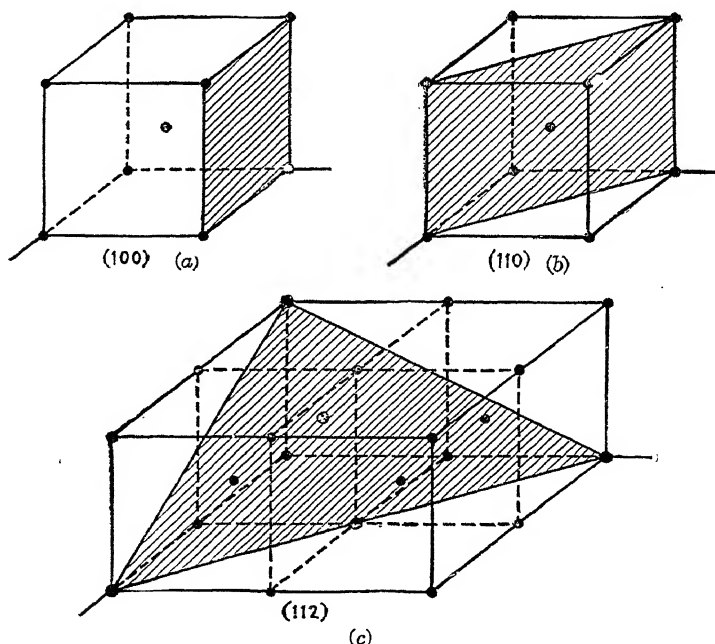
Fig. 33.—The location of the principal planes in a body-centered cubic lattice. (*Smithells.*)

in or parallel to the plane of two principal axes and cuts the third at a distance equal to the length of the edge of the unit cell, as shown in Fig. 33. The intercepts of this plane are, therefore, 1, ∞, ∞ and the indices are $1/1$, $1/\infty$, $1/\infty$ or 1, 0, 0. This is usually written (100) when referring to the specific plane in question, or {100} when referring generally to planes of this form and [100] when a direction perpendicular to the plane is indicated. The other cube faces have indices (010) and (001). Similarly, the diagonals that bisect the cube faces are the (110), (101), and (011) planes, and so on, as shown in Fig. 33. The (112) plane is shown in Fig. 33c.

If, d is the distance between two parallel planes in a cubic lattice, the indices of the planes being $h_1h_2h_3$, and the length of the cube edge a, then $d = a/\sqrt{h_1{}^2 + h_2{}^2 + h_3{}^2}$. From this it follows that the interplanar distance is less, the larger the values of the indices. The separation of cube faces would be a, that of the octahedral planes, $a/\sqrt{3}$ and of the dodecahedral planes, $a/\sqrt{2}$.

Stereographic projection is a most useful method of defining the location of planes in two-dimensional form. A sphere is circumscribed about the crystal, as in Fig. 34. A line normal to the crystal plane in question and passing through the center of the sphere will intersect the surface of the sphere. The lines
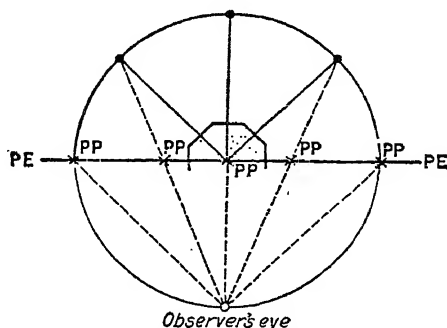
FIG. 34.—Stereographic projection to locate crystal planes. (*Niggli.*)

joining these intersections and the "south pole" of the sphere, or the focal point, pierce the plane PE at points PP. These points on the equatorial plane PE represent the corresponding planes of the crystal. By this means the location of certain planes, especially during the process of deformation of a poly-crystalline mass, is greatly facilitated. It leads to the so-called *pole figures* described on page 107.

The Interference of Light Waves.—If a train of light waves, as shown in Fig. 35, is allowed to fall upon a diffraction grating, the separation of the openings in the grating being of the order of the wave length of light, then each opening in the grating becomes the center of a new train of waves. Where the emergent new wave trains are in phase, *i.e.*, where the crests and valleys of the emergent waves coincide, intensification of light will occur. This is shown by the heavy lines indicating the new wave fronts

of the first and second order in the figure below.   In directions between these, *i.e.*, where the crests of one wave train coincide with the valleys of another, no light exists.   Interference has extinguished it.[1]

The Nature of X Rays.—If, in an evacuated tube, such as is shown in Fig. 36, with a potential of some 30,000 volts across the electrodes, electrons are emitted from a separately heated glowing filament at the cathode, as in the Coolidge tube, these electrons will "fall" through the potential gradient toward the anode
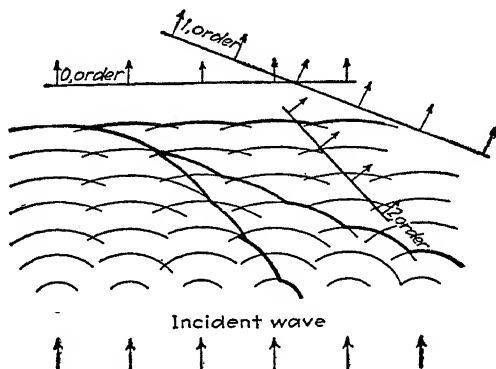
FIG. 35.—Origin of diffracted wave trains at a line lattice.   (*Ewald.*)

(or "anticathode").   If they attain sufficient velocity, they will impinge on the atoms at the surface of the anticathode, often of copper or molybdenum, and disturb the electrons in the outer and inner orbits of these atoms.   The readjustment following this electronic disturbance is accompanied by a release of energy from the bombarded atoms in the form of an electromagnetic wave, similar in nature to light but of wave length about 10,000 times shorter than that of visible light, *i.e.*, from 0.25 to 0.1 $\times$ 10^{-8} cm. (1 $\times$ 10^{-8} cm. = 1 Ångström).   Ordinarily these X rays will vary in wave length from each other and, therefore, correspond to "white light" in the range of visible radiation.   Under proper

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[1] A demonstration that illustrates the principle of diffraction very simply may be performed by placing in an ordinary projection lantern a card with a pinhole in it, thus throwing a narrow pencil of light rays on the screen. If a piece of ordinary bolting cloth be stretched over a frame and held in the path of the rays, diffraction will cause four additional images of the pinhole to appear on the screen.   This pattern should be compared with that of Fig. 40 produced by holding a crystal (lattice) in a beam of X rays, as in Fig. 36.   The crystal serves as diffraction grating for the invisible X rays.

conditions of voltage, anode or target material, and filtration, a beam of rays containing a preponderance of waves of a certain length, the "characteristic radiation" of the target, may be obtained. These are the rays commonly used in crystal analysis. The characteristic radiation of a molybdenum target for example is

$$\alpha_1 = 0.712 \text{ Å.}, \ \alpha_2 = 0.708 \text{ Å.}$$

The Laue Method.—Professor von Laue, at Zurich, speculating upon the then unknown nature of X rays decided that *if* the atoms in a crystal were arranged in parallel layers, the distance apart of these layers would be of about the right dimensions to form a diffraction grating for X rays, *if* X rays actually were electromagnetic waves. Fried-rich and Knipping, his associates, used "white" X rays and a careful positioned crystal of zinc sulphide and, after many attempts, finally obtained a geometrical diffraction pattern on a photographic film behind the crystal, as shown, because of its historical significance, in Fig. 40. His experiment indicated first,

FIG. 36.—The Laue method. (*Ewald.*) (NOTE: In X-ray bulb, upper c = cathode; lower c_1 = anticathode; c at right = crystal.)

that X rays are electromagnetic waves, and second, that the arrangement of the atoms in a crystal is orderly and of such dimensions as to supply a convenient diffraction grating for these rays.

Figure 36 shows the principle of the Laue method diagrammatically. White X rays pass through a diaphragm, D, to produce a narrow beam and fall on a carefully mounted single crystal, C, free from internal stress, which acts as a diffraction grating. The crystal singles out that wave length of the primary beam which for the setting of the crystal satisfies Bragg's law.[1] The primary ray, P, and the diffracted rays, S and S', register on the photographic plate behind the crystal. If the characteristic wave length of the primary ray is known by previous calibration, the distances between the reflecting planes in the crystal can be

[1] See pp. 50 and 51.

calculated. This method is not widely used today because of the difficulties in obtaining perfect, stress-free crystals, and because of certain ambiguities in the results it yields.
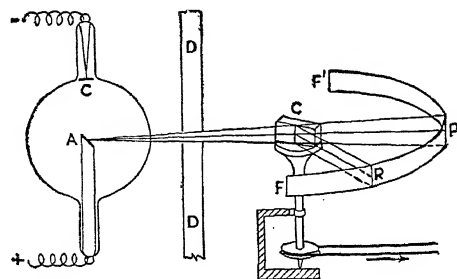
Fig. 37.—The Bragg method.   (*Ewald.*)

The Bragg Method.—A year later, in England, the Braggs (father and son) demonstrated that the interference patterns from crystals could be explained by the *reflection* of the primary ray from the lattice planes of the crystal. It soon became apparent that this conception was quite analogous to the explanation given by von Laue and was more convenient.
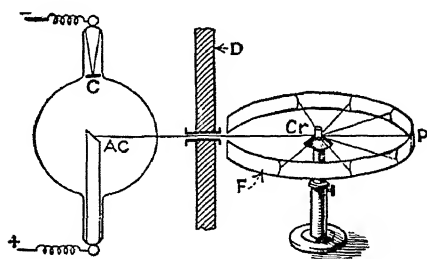
Fig. 38.—Hull or Debye and Scherrer method.   (*Ewald.*)

The conditions for reflection of an X-ray beam from the planes of a single crystal are not so simple as those for reflection of visible light as, for instance, from a mirror. While a mirror reflects light reaching it from *any* angle, X rays will be reflected from a crystal only under a certain set of conditions. These conditions are given by the Bragg equation

$$n\lambda = 2d \sin \theta$$

when n is any small integer, λ is the wave length of the ray, d is the interplanar distance of the set of reflecting planes in the

crystal, and θ is the angle which the incident beam makes with the reflecting planes. The derivation is simple: In Fig. 39 if AA' is the incident train of waves of wave length λ, then the condition for reflection is obviously that the waves shall be in phase with each other when they leave the crystal, *i.e.*, the additional distance *cbe* traversed by wave A' must be a positive integer of the wave length, or $n\lambda$. Since $\sin \theta = cb/d$, it follows that $cb = d \sin \theta$ and $cb + be = 2d \sin \theta$. The extra distance *cbe* equals $2d \sin \theta$. If λ is known (characteristic wave length of the target), then θ, the angle at which reflection is obtained, can be measured and d can be calculated.

Confirmation of the value of d, involving the choice of n, may be found in the following way. Suppose d for one set of planes in a copper crystal comes out as 3.60 Å. or multiple thereof, and
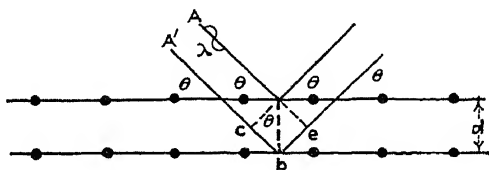
FIG. 39.—Reflection of X rays from a crystal lattice. (*Bragg.*)

the diffraction pattern indicates the face-centered cubic arrangement. The face-centered cubic lattice contains one atom at each of its eight corners, but each corner atom is shared by *eight* adjacent cubes,[1] so that really only one-eighth of the eight corner atoms or one atom belongs to the one cube. The six atoms in the cube faces are shared by two adjacent cubes each, so that one-half of these six face atoms or three belong to the cube, making a total of four atoms per unit cell. Cells of this size, 3.60×10^{-8} cm. would be found in a cube 1 cm. on an edge to the number of $1/(3.60 \times 10^{-8})^3 = 21.42 \times 10^{21}$. The total number of atoms in 1 cc. would thus be $4 \times 21.42 \times 10^{21} = 85.68 \times 10^{21}$ atoms per cubic centimeter. The weight of a copper atom is 63.57 times the weight of a hydrogen atom (which is 1.64×10^{-24} g.). The weight of 1 cc. copper would, therefore, be

$$85.68 \times 10^{21} \times 63.57 \times 1.64 \times 10^{-24} = 8.933 \text{ g.,}$$

which is quite close to the measured density of copper and indi-

[1] See also p. 23.

cates that the parameter calculated from the chosen value of $n = 1$, is correct.

A schematic illustration of the Bragg method is shown in Fig. 37.   Monochromatic X rays are used, and the carefully mounted,
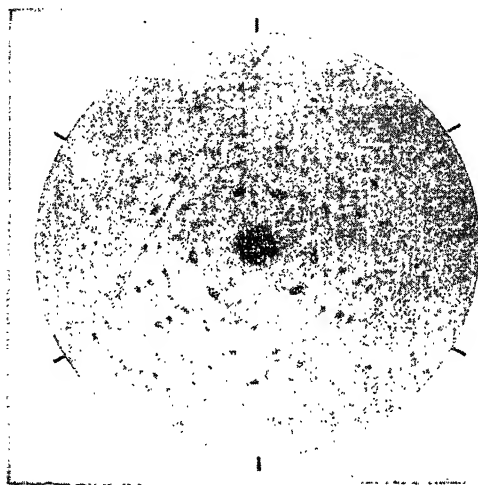
Fig. 40.—Diffraction pattern of zinc sulphide along an axis of threefold symmetry (body diagonal of the cube).   (*von Laue, Friedrich, and Knipping.*)

stress-free crystal is rotated in the beam of X rays.   As each set of planes makes its proper angle θ with the beam and satisfies Bragg's law, a reflection is obtained and registered on the film, F. An interference pattern for a tin crystal is shown in Fig. 41.   The

Fig. 41.—Layer line diagram of a tin crystal.   (*Polanyi.*)

Braggs did not use a film to record the reflection, but a chamber containing a gas (methyl iodide) which ionizes readily when a reflected beam enters the chamber.   The ionization of the gas permitted a current to flow through the chamber, and the magnitude of this current was recorded by an ammeter for the different angles of rotation.   The Bragg method with its recent modifica-

tions offers one of the most accurate and exhaustive means for crystal analysis.

The Powder Method.—The greatest usefulness of the X-ray method in metallurgy resulted from the simultaneous discoveries of Hull in America, and of Debye and Scherrer in Europe. They found that if a large number of very small crystals, as in a crystalline powder or in a fine-grained metallic wire, were exposed to a beam of monochromatic X rays, chance would provide enough crystals in exactly the proper position with respect to the rays to satisfy Bragg's law for all planes. (If a pin, representing the beam of rays, be stuck through a small cube of rubber, representing a crystallite, at the proper angle θ for reflection from one set of planes, and the pin be rotated on its own axis, the cube will pass through all the positions in which these planes will reflect, and these reflections will form a cone of rays, the intersection of this cone with a flat film producing a circle.) Not only is this condition established for one set of planes in the crystallites but for all sets. The reflections from each set of planes will form a *cone* of rays. The section of this cone on the curved film, *F*, shown in Fig. 38 will be curved lines. A film for powdered or polycrystalline copper is shown in Fig. 42. Monochromatic light is used as in the Bragg method, but rotation of the specimen is, of course, unnecessary.

This method, because it does not require the preparation of a single crystal specimen but can use a metallic aggregate, as for example an ordinary wire or sheet of metal containing crystalline grains in a more or less random orientation, is of the greatest usefulness in metallurgy. With it, entire metallic objects or representative parts of them, such as wires, sheets, and welds, may be examined.

Some Results of X-ray Studies.—In addition to revealing the structure of metallic crystals as

Fig. 42.—Powder pattern for copper.

described above, the powder method has made it possible to study the *orientation* of the crystallites in the specimen.   In a chilled casting or in a severely deformed object, such as a thin wire or sheet, the grains are not oriented at random but, to a greater or less extent, are aligned with respect to the surface of the piece. An object in this condition is said to possess a fibered structure.[1]
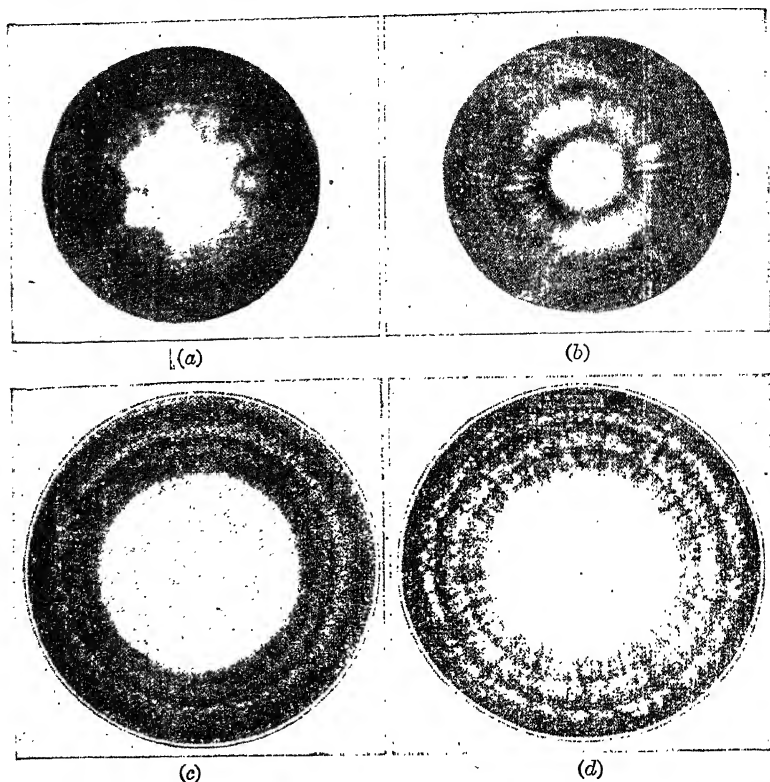
Fig. 43a–d.—(a) Powder pattern of cold-rolled copper sheet, X rays perpendicular to direction of rolling; (b) same but parallel thereto; (c) fine-grained aluminum alloy; (d) coarse-grained, corrosive aluminum alloy.   (*Clark.*)

The interference pattern of a rolled copper sheet is shown in Fig. 43a, with the X rays perpendicular to the direction of rolling. The crystallites in the sheet have taken up a preferred orientation with respect to the axis of the wire as represented by those spots, and the positions intermediate between them are almost entirely

[1] See also pp. 103 *ff.* for a discussion of fiber structure.

deserted.   Figure 43b shows the pattern parallel to the direction of rolling.   *Grain size* also is revealed by X-ray methods.   Figure 43c shows the powder photograph of a fine-grained aluminum alloy.   Figure 43d shows that of a coarse-grained aluminum alloy.

The circles of reflection in 43d are no longer continuous but consist of widely separated spots.   Figures 43c and 43d indicate that in these particular specimens the crystallite orientation was truly random, but that the number of crystallites was too small in both specimens to permit representation of all the reflecting positions to give complete circles. Such a result indicates that the grain size of the specimen is large.
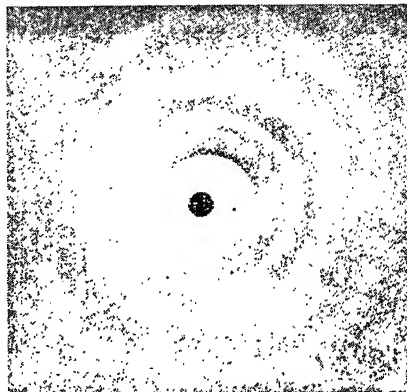
FIG. 43(e).—Very fine grained tungsten. (*Smithells.*)

If the grain size of the specimen is between 10^{-3} and 10^{-6} cm., the interference rings will be sharply defined.   If the grain size is smaller than 10^{-6}, the rings will be diffuse as shown in Fig. 43e.
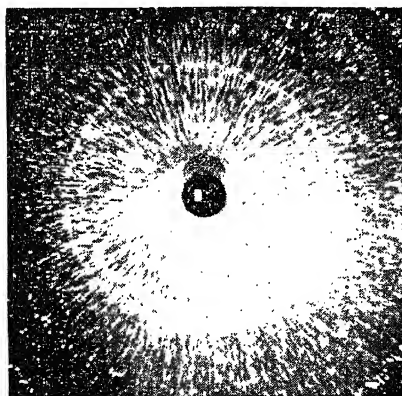
FIG. 43(*f*).—Pattern of Armco iron, showing asterism due to internal (*Carl Bittrich.*)

From the thickness of the rings can thus be estimated the size of the grains composing the object.

The presence of *internal stresses* in a metallic object is revealed by a radial appearance, called *asterism*, in the interference pattern of "white" X rays, as shown in Fig. 43f, for an Armco iron wire.   Apparently the lattice planes have been bent and reflect as spherical mirrors.   Another hypothesis supposes that the uniformity of the interplanar distance has been disturbed.   The width of the diffraction lines also has been used as a measure of the intensity

of the internal stress. The detection of internal stress in metallic objects is of great practical importance to their safety in engineering work (see page 112).

The positions and spacings of the atoms in the crystals of a number of pure metals are given in Table III.

Electron Diffraction.—A comparatively new tool for metallurgical research is the electron-diffraction camera. The development dates from 1927, when C. J. Davisson and L. H. Germer of the Bell Telephone laboratories, and, independently, G. P. Thomson in England succeeded in diffracting a stream of electrons from a crystal. Electrons in motion under a voltage potential act like a train of waves and are diffracted from a crystal in the same manner as X rays, indicating, on a similar diffraction pattern, interatomic distances, orientation, grain size, and stress. The principal difference between them is that (1) electron waves penetrate only a few hundred Ångström units, or about two-millionths of an inch, while X-ray penetration is measured in ten- to hundred-thousandths of an inch; and (2) the photographic exposures of the electron-diffraction patterns are only a matter of a fraction of a second, compared to the hours required by X rays. The wave length of electron waves is determined by the formula $\lambda = \sqrt{150 \div V}$ Å units, where V is the accelerating voltage applied to the electron source. The source is either a hot filament, as used in the generation of X rays, or a gas chamber similar in type to a modern neon sign. The voltages applied vary from 30 to 70 kv.

The fact that the penetration of electrons is of the order of millionths of an inch, compared to ten- to hundred-thousandths of an inch for X rays, indicates their usefulness. They may be used to investigate very thin surface films of even submicroscopic dimensions and are diffracted by very small amounts of material. They may thus be used to determine the composition of thin surface layers, such as oxide films; they may be used to determine the manner in which the lattice between two crystallographically dissimilar metals varies when one is bonded to the other; and they may be used to investigate the effect of deformation or polishing upon the crystallinity of the disturbed surface layers of the metal concerned. These are just a few of the present uses of the new tool, and the future seemingly presents many more

possibilities, such as the investigation of submicroscopic inclusions in metals, and perhaps even the investigation of grain boundary conditions in polycrystalline metals.

Summary.—The internal structure of solidified metal objects is a conglomerate of variously oriented crystalline grains. Although the external form is irregular, the interior of each grain is truly crystalline. The layers of atoms in a crystal act as planes, and the location of these planes can be conveniently represented by referring them to space coordinates.

These planes in the crystal lattice will reflect X rays or electron waves (actually it is the atoms that reflect the waves) and from such reflections can be calculated the interatomic distances and the type of crystal structure. Electron waves penetrate only the surface layers and are useful for the investigation of thin films. Knowledge of the interatomic distances, of the grain size of the material, of the orientation of the grains in the body, and of the presence of internal stress also may be gained by the use of X rays and electron diffraction.

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TABLE III.—Physical Constants and Properties of the Metals

	Element	Atomic number	Crystal system	Lattice coordinates, Å	Atomic weigh, gr.	Melting point, C.	Boiling point, C.	Sp. gr.	Atomic volume cm³/g. atom.	Latent heat of fusion cal./gr.	Linear coefficient of ex. (x 10⁻⁶)	Closest approach of atoms, Å	Sp. ht., cal./gr./°C	Electric resistance microohm-cm.	Elect. atomic conductivity
Group I(a)	Li	3	B.C.C.	a = 3.51	6.94	186	1336	0.534	13.1	32.81	56	3.0	0.79	8.5	16
	Na	11	B.C.C.	a = 4.30	22.997	97.5	880	0.971	23.7	27.53	71	3.72	0.295	4.6	95
	K	19	B.C.C.	a = 5.33	39.096	62.3	760	0.86	45.5	14.5	83	4.62	0.177	7.0	142
	Rb	37	B.C.C.	a = 5.70	85.48	38.5	700	1.53	55.87	6.005	90	4.9	0.0802	12.5	130
	Cs	55	B.C.C.	a = 6.20	132.91	28.5	670	1.90	69.95	3.76	97	5.3	0.0521	20.0	124
Group II(a)	Be	4	C.P.H. Dist.	a = 2.281 c = 3.577	9.02	1278	1530	1.85	4.96	345.5	12.3	2.22	0.425	18.5	8
	Mg	12	C.P.H.	a = 3.2022 c = 5.1991	24.32	650	1110	1.74	14.0	70	25.7	3.190	0.249	4.46	43
	Ca	20	F.C.C.	a = 5.56	40.08	850	1439	1.55	25.86		25	3.93	0.157	4.6	81
	Sr	38	F.C.C.	a = 6.075	87.63	800	1150	2.6	33.7	25		4.30	0.068	22.76	35
	Ba	56	B.C.C.	a = 5.015	137.36	850	1140	3.5	39.25			4.34			14
Group III(a)	Al	13	F.C.C.	a = 4.0413	26.97	658.7	1800	2.70	9.99	93	24	2.858	0.2259	2.655	58
	Sc	21	C.P.H. Dist.		45.10	1200	2400	2.5	18						
	Y	39	C.P.H. Dist.		88.92	1490	2500	5.51	16.13			3.50			
	La	57	C.P.H. Dist.	a = ... c = ...	138.92	885	1800	6.15	22.6	93		3.7	0.0446	50.0	11
Group IV(a)	Ti	22	C.P.H. Dist.	a = ... c = ...	47.90	1800	>3000	4.5	10.6		7.14	2.90	0.142		2
	Zr	40	C.T.H. Dist.	a = ... c = ...	91.22	1700	>2900	6.4	14.6		6.3	3.16	0.066	.41	6
	Hf	72	C.P.H. Dist.	a = ... c = ...	178.6	2207	>3200	1.4	15.66			3.14			10
Group V(a)	V	23	B.C.C.	a = 3.034	50.95	1715	3400	5.68	8.7		7.2	2.627	0.1153	26	13
	Cb	41	B.C.C.	a = 3.294	92.91	1950	>3300	8.57	10.5		6.5	2.852	0.0356	20	16
	Ta	73	B.C.C.	a = 3.269	180.88	2850	>4100	16.6	10.9			2.854		15.5	
Group VI(a)	Cr	24	B.C.C.	a = 2.876	52.01	1615	2200	7.14	7.31	31.75	8.1	2.492	0.12	13.1	44
	Mo	42	B.C.C.	a = 3.143	95.95	2620	3700	10.2	9.40	44	5.49	2.720	0.0647	4.77	37
	W	74	B.C.C.	a = 3.155	183.92	3370	4727	19.3	9.53	44	4.0	2.734	0.034	5.48	34
Group VIII(b)	Ru	44	C.P.H.	a = ... c = ...	101.7	2450	4150	12.2	8.33		8.5	2.644	0.061	10	13
Group VIII(b)	Rh	45	F.C.C.	a = 3.7647	102.91	1985	>2500	12.44	8.23		8.9	2.684	0.0598	4.93	38
	Pd	46	F.C.C.	a = 3.8817	106.7	1550	2200	12.0	8.9	34.2	11.60	2.744	0.0587	10	21
Group VIII(c)	Os	76	C.P.H. Dist.	a = ... c = ...	190.2	2700	4450	22.5	8.45		5.70	2.67	0.031	9	25
	Ir	77	F.C.C.	a = 3.8312	193.1	2440	4400	22.4	8.6		6.41	2.709	0.0322	6.08	43
	Pt	78	F.C.C.	a = 3.9158	195.23	1755	4050	21.45	9.1	27.1	8.8	2.768	0.0319	9.83	27

Group	No.	Element	Structure	Lattice constants	At. wt	m.p.	b.p.							89×10^4	
Group IV(b)	32	Ge	Diamond cubic	a = 5.647	72.60	958	volatilizes 2700	5.36	13.54	......	......	2.44	0.0733	11.5	.....
	50	Sn	B.C.T.	a = 5.8194, c = 3.1753	118.7	231.9	2270	7.30	16.23	14.4	22.4(∥) 46.4(⊥) 29.5	3.016	0.054	20.65	59
	82	Pb	F.C.C.	a = 4.9389	207.2	327.5	1620	11.34	18.3	6.26	23	3.4922	0.030	......	42
Group VII(a)	25	Mn	Cubic (complex)	a = 8.894	54.93	1260	1900	7.44	7.4	64.8		1.065	0.107		33
	43	Ma	C.P.H.	..... a = 2.755, c = 4.449	186.31	2300	5870(?)	20	8.9	......	12.5(∥) 4.7(⊥)	2.7349	0.0346	21	.....
	75	Re				3440									.....
Group VIII(a)	26	Fe	B.C.C.	a = 2.861	55.84	1535	3000	7.86	7.10	65.0	11.9	2.478	0.1075	9.8	13
	27	Co	C.P.H. Dist.	a = 2.500, c = 4.070	58.94	1480	2900	8.8	6.6	58.38	12.08	2.50	0.0989	9.7	20
	28	Ni	F.C.C.	a = 3.517	58.69	1452	2900	8.9	6.64	73.8	13.7	2.487	0.112	6.9	19
Group I(b)	29	Cu	F.C.C.	a = 3.608	63.57	1083	2310	8.94	7.11	50.6	16.42	2.551	0.0918	1.682	104
	47	Ag	F.C.C.	a = 4.0774	107.810	960	1950	10.50	10.27	24.3	18.4	2.882	0.0558	1.62	192
	79	Au	F.C.C.	a = 4.07	197.2	1063	2600	19.3	10.22	16.11	14.4	2.878	0.0308	2.42	176
Group II(b)	30	Zn	C.P.H.	a = 2.659, c = 4.936	65.38	419.4	907	7.14	9.16	24.09	29.8	2.658	0.09	6.2(∥) 5.8(⊥)	49
	48	Cd	C.P.H.	a = 2.9727, c = 5.606	112.41	320.9	778	8.65	12.99	13.17	29.8	2.972	0.0547	7.59	63
	80	Hg	Rhomb.	a = 2.999, α = 70°31.7′	200.61	−38.87	356.9	13.55	14.8	2.06	57.0	......	0.0332	95.8	35
Group III(b)	31	Ga	Ortho-rhomb.	a = 4.506, b = 4.506, c = 7.642	69.72	29.75	2000	5.91	11.82	19.16	18.3	2.447	0.0788	57.1	13
	49	In	F.C. Tetra.	a = 4.585, c = 4.941	114.76	156.4	>1450	7.31	15.7	......	33.0	3.24	0.0508	9	77
	81	Tl	C.P.H. Dist.	a = 3.450, c = 5.520	204.39	305	1650	11.85	17.24	7.185	28.0	3.40	0.0311	18.1	46
	33	As	Rhomb 8N	a = 4.135, α = 54°75′	74.91	Sublimes, 500°C, under pres. 630°C	615°C	5.73	13.07	Volatilizes	8.86	2.50	0.0622	35	8
Group V(b)	51	Sb	Rhomb 8N	a = 4.4974, α = 57°6′	121.76	630°C	1635°C	6.62	18.39	33.26	11.20	2.878	0.0493	39	12
	83	Bi	Rhomb 8N	a = 4.736, α = 57°14′	209.0	271°C	1450°C	9.80	21.33	12.40	13.45	3.104	0.0290	115	9
Group VII(b)	34	Se	Hex.	a = 4.337, c = 4.944	78.96	217	688	4.81	16.4	......	37.0	2.32	0.084	12	...
	52	Te	Hex.	a = 4.445, c = 5.912	127.61	452	1390	6.24	20.45	7.305	16.8	2.86	0.0468	....	...
	84	Po	Monoclinic	a = 7.42, b = 4.20, c = 14.10	Approx. 210	......	......			......	......	2.81			...

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TABLE III.—PHYSICAL CONSTANTS AND PROPERTIES OF THE METALS.—(Continued)

Element	Thermal conductivity, cal./cm./°C./sec.	Compressibility $x \cdot 10^{-7} = \frac{1}{v}\cdot\frac{dv}{dp}$	Characteristic temp. θ	E.m.f.	Young's modulus in p.s.i. $\times 10^6$	Brinell hardness	Coordination number	Electron shells	Electrons free atom	Atomic heat, cal./gr. atom	Electrochemical equivalent	Specific magnetic susceptibility $X\times 10^6 = \frac{2F}{AlP^2}$	Goldschmidt's atomic diameters
Group I(a)													
Li	0.17	87	494	+2.9595	....	....	8	K-L	2-1	5.48	0.07192	+0.5	3.13
Na	0.325	156	226.5	+2.7146	....	0.07	8	K-L-M	2-8-1	6.78	0.33832	+0.6	3.83
K	0.237	357	132	+2.9241	....	0.037	8	K-L-M-N	2-8-8-1	4.57	0.40516	+0.5	4.76
Rb	....	520	83	+2.9259	....	....	8	K-L-M-N-O	2-8-18-8-1	6.77	0.88542	+0.2	5.02
Cs	....	700	60	....	....	....	8	K-L-M-N-O-P	2-8-18-18-8-1	6.92	1.87632	+0.1	5.40
Group II(a)													
Be	0.3847	7.8	1060	+1.69	42.7	(Drawn and annealed 29.4)	6(6)	K-L	2-2	3.58	0.64678	-1.0	2.25
Mg	0.370	29.5	350	+2.40	6.25	17	6(6)	K-L-M	2-8-2	....	....	....	3.20
Ca	....	57.0	244	+2.87	....	....	12	K-L-M-N	2-8-8-2	5.8	0.20422	+0.55	3.93
Sr	....	82	148	+2.92	....	....	12	K-L-M-N-O	2-8-18-8-2	6.21	0.43106	+1.10	4.29
Ba	....	102	116	+2.90	....	(annealed 16)	8	K-L-M-N-O-P	2-8-18-18-8-2	9.34	0.71173	+0.9	4.48
Group III(a)													
Al	0.52	13.4	374	+1.7	10	....	12	K-L-M	2-8-2,1	6.09	0.09316	+0.58	2.80–2.85
Sc	....	....	....	....	....	....	6	K-L-M-N	2-8-8,1,2	....	0.15529	....	....
Y	....	35	152	....	....	37	6(6)	K-L-M-N-O	2-8-18,8,1,2	....	0.30719	+1.04	3.62
La	....	....	....	....	....	....	12	K-L-M-N-O-P	2-8-18-18,8,1,2	6.19	0.47391	....	3.745
Group IV(a)													
Ti	....	8	396	....	....	....	6(6)	K-L-M-N	2-8-8,2,2	6.70	0.12110	+1.25	2.93
Zr	....	11	275	....	....	....	6(6)	K-L-M-N-O	2-8-18,8,2,2	6.02	0.23633	-0.45	3.19
Hf	....	9	213	....	....	....	6(6)	K-L-M-N-O-P	2-8-18-32,8,2,2	6.02	0.16271	....	3.17
Group V(a)													
V	0.130	6.1	413	....	27	....	8	K-L-M-N	2-8-8,3,2	6.04	++ 0.16502	+1.4	2.69
Group V(a)													
Cb	....	5.7	301	....	....	....	8	K-L-M-N-O	2-8-18,8,3,2	6.01	+++	+1.3	2.94
Ta	....	4.8	263	....	....	....	8	K-L-M-N-O-P	2-8-18-32,8,3,2	6.17	+++ 0.37618	+0.87	2.94
Group VI(a)													
Cr	0.165	6.1	457	.557	....	91	8	K-L-M-N	2-8-8,5,1	6.39	+++ 0.08983	+3.6	2.57
Group VI(a)													
Mo	0.350	3.6	357	....	50.2	(drawn 147)	8	K-L-M-N-O	2-8-18,8,5,1	6.22	+++ 0.16581	+0.04	2.80
W	0.476	3.2	315	....	60.0	....	8	K-L-M-N-O-P	2-8-18-32,8,4,2	6.15	+++ 0.31799	+0.28	2.82
Group VIII(b)													
Ru	....	3.4	426	....	....	(cast 220)	6(6)	K-L-M-N-O	2-8-18,8,7,1	5.6	+ 1.05392	+0.43	2.67
Rh	0.213	3.6	315	....	42.5	(cast 139)	12	K-L-M-N-O	2-8-18,8,8,1	6.06	+ 1.06646	+1.08	2.684
Pd	0.161	5.3	270	-0.820	17.0	(drawn 49)	12	K-L-M-N-O-P	2-8-18,8,10	5.74	+ 1.10574	+5.24	2.745

Group	El.								Shells	Config				
Group VIII(c)	Os	.....	.....	256	.....	.....	.....	6(6)	K-L-M-N-O-P	2-8-18-32-8,6-2	5.92	++1.9727	+0.05	2.70
	Ir	0.141	2.7	247	.....	74.7	(cast 172)	12	K-L-M-N-O-P	2-8-18-32-8,7-2	5.93	++2.00111	0.13	2.709
	Pt	0.166	3.6	212	−0.863	21.4	(drawn 64)	12	K-L-M-N-O-P	2-8-18-32-8,8-2	6.19	n 2.02318	+1.02	2.709
Group IV(b)	Ge	.....	13.8	.....	.....	.....	(hard drawn) 10	4	K-L-M-N	2-8-18-2,2	5.33	+++0.18809	−0.12	2.788
	Sn	0.157	8.8	111	0.136	5.9-7 8	10	4(2)	K-L-M-N-O	2-8-18-18-2,2	6.40	+++0.30752	−0.40	.....
	Pb	0.083	23.7	89	0.122	2.56	4.2	12	K-L-M-N-O-P	2-8-18-32-18-2,2	6.22	+++0.53686	−0.12	3.494
Group VII(a)	Mn	.....	7.9	368	1.10	.....	.....	8	K-L-M-N	2-8-8,5-2	5.89	1.13848	+7.5	.....
	Ma	.....	.....	310	.....	.....	.....	6(6)	K-L-M-N	2-8-18-8,6-1	.....	1.95551	+0.37	.....
	Re	.....	.....	.....	.....	.....	.....	.....	K-L-M-N	2-8-18-32-8,5-2	6.07	.....	.....	2.75
Group VIII(a)	Fe	0.19	5.94	407	+++0.441 / +0.045 / +0.278 / +0.231	26-29	(electrolytic 77)	8	K-L-M-N	2-8-8,6-2	7.70	++0.28934	>	.....
Group VIII(a)	Co	0.105	5.4	317	.....	.....	(cast 124)	6(6)	K-L-M-N	2-8-8,7-2	0.80	+++0.30540	>>	2.50
	Ni	0.140	5.3	425	.....	30	(cast 90-110 at 99°)	12	K-L-M-N	2-8-8,8-2	8.23	++0.30410	>>	2.487
Group I(b)	Cu	0.923	7.2	329	−0.470	16	(annealed 32-35)	12	K-L-M-N	2-8-18-1	5.775	+0.65880	−0.080	2.551
	Ag	0.974	9.0	210	−0.7078	10.3	(cast 40)	12	K-L-M-N-O	2-8-18-18-1	5.077	+1.11800	−0.20	2.883
	Au	0.7072	9.8	164	−0.150	11.3	(cast 25)	12	K-L-M-N-O-P	2-8-18-32-18-1	6.16	+2.04359	−0.15	2.877
Group II(b)	Zn	0.208	16.9	213	0.7081	11.4	(rolled 17.1-42)	6(6)	K-L-M-N	2-8-18-2	5.25	+++0.33877	−0.157	2.748
	Cd	0.217	22.5	134	0.401	10.6	(cast 12.05)	6(6)	K-L-M-N-O	2-8-18-18-2	5.46	+0.58245	−0.18	3.042
	Hg	0.020	37	54	−0.3992	.....	.....	6	K-L-M-N-O-P	2-8-18-32-18-2	6.61	1.03947	−0.19	3.10
Group III(b)	Ga	0.057	20	125	0.50	.....	.....	4(8)	K-L-M-N	2-8-18-2,1	5.50	+++0.34084	−0.24	3.188
	In	.....	25	106	0.336	11.3	.....	4(8)	K-L-M-N-O	2-8-18-18-2,1	6.52	+++0.39659	−0.11	3.42
	Tl	0.00315	34.8	88	0.330	4.6	.....	6(6)	K-L-M-N-O-P	2-8-18-32-18-2,1	6.36	+++0.70604	−0.24	.....
Group V(b)	As	.....	44	224	−0.30	.....	147	3(3)	K-L-M-N	2-8-18-2,3	6.17	+++0.25894	−0.31	.....
	Sb	0.0444	27	142	−0.10	11.3	.....	3(3)	K-L-M-N-O	2-8-18-18-2,3	6.01	+++0.42062	−0.87	3.228
	Bi	0.0200	29.2	80	−0.226	4.6	.....	3(3)	K-L-M-N-O-P	2-8-18-32-18-2,3	6.08	+++0.72196	−1.35	3.64
Group VI(b)	Se	.....	11.8	135	.....	.....	.....	2(4)	K-L-M-N	2-8-18-2,4	6.625	+++0.20519	−0.32	.....
	Te	0.01433	50.8	120	−0.558	27	.....	2(4)	K-L-M-N-O	2-8-18-18-2,4	5.98	+++0.33032	−0.31	.....
	Po	.....	.....	.....	−0.40	.....	.....	.....	K-L-M-N-O-P	2-8-18-32-18-2,4	.....	.....	.....	.....

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CHAPTER II

THE PHYSICAL PROPERTIES OF METALS. THEIR CHANGE WITH TEMPERATURE

Introduction.—A complete discussion of the physical properties of metals should include the mechanical properties—strength, and formability, as well as such physical properties as density, thermal expansion, atomic heat, and electrical conductivity. However, because of the fact that the mechanical properties are so important, being involved in most processes of fabrication and industrial applications of metals, they merit detailed consideration in a separate chapter. The important physical properties other than the mechanical properties will be dealt with here.

Table III, pages 60 to 63, is a compilation of the important physical properties of the metals, the order of the metals following the subgroups of the periodic chart as presented in the Introduction (Table I, page 5). When examined in this order, many of the properties exhibit a periodicity related to the grouping, and many of the properties may be accounted for in terms of the valence or free electrons in the metal lattice, as will be shown in the subsequent consideration of individual properties.

When the periodic chart of Mendelejeff was first drawn up, the elements were arranged in horizontal rows following the order of increasing atomic weight, so that elements with generally similar properties fell beneath each other in vertical rows. In 1895 Julius Thomson presented another grouping, which is more convenient for studying metallic properties. A chart of this general type is shown in Table I in the Introduction. In this grouping, if each vertical row is divided into two subgroups (*A* and *B*), it will be found that the metals in each subgroup have markedly similar properties.

Density.—Density is defined as the weight per unit volume of a substance. The examination of the property table will show that density increases regularly with increasing atomic number in each subgroup. There are two ways of determining the den-

sity of metals. One is by determining the difference in weight of a unit volume of metal when suspended in two different media of known density. The other, and more accurate, means of density determination for crystalline substances is by the use of X rays, as was indicated on pages 51 and 53. The X-ray density is the true density, for it is not influenced by inhomogeneities such as porosity and insoluble nonmetallic inclusions. The reciprocal of the density is the specific volume, $1/d$ or v.
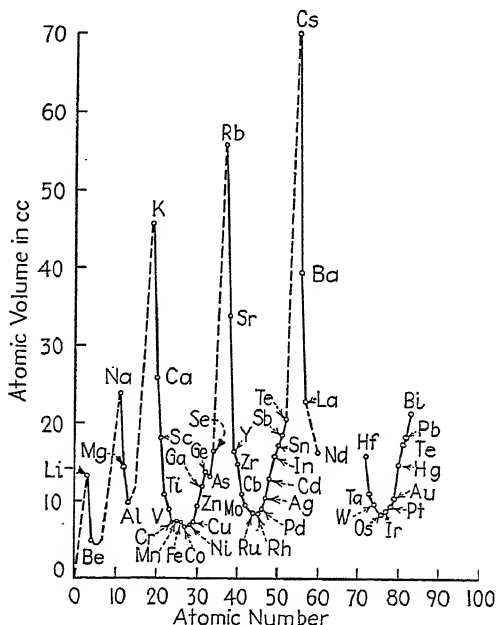
Fig. 44.—Periodic variation of atomic volume with atomic number.

From the linear coefficient of expansion and the specific volume, the effect of temperature on density may be determined, and the density may be calculated at any desired temperature. The increasing use of the light metals, aluminum and magnesium, may indicate the importance of density in engineering design, particularly for moving parts.

Atomic Volume.—From the atomic weight and the density a useful concept, the atomic volume, may be calculated which is fundamental in that many physical properties may be related to it. $V_{at} = A/d$, where V_{at} is the atomic volume, A is the atomic weight, and d is the density. When V_{at} is plotted against the

atomic number (see Fig. 44), a series of maxima and minima are exhibited which resemble those obtained when other atomic properties are plotted against the atomic number. It will be noticed that within each subgroup the atomic volume increases with increasing atomic number. This increase in atomic volume is to be expected from the consideration of the increase in the number of orbital electrons that must be held around each nucleus.

Compressibility.—The compressibility of metals is determined by measuring the decrease in volume of a unit volume of a metal under pressure exerted in a confining cylinder. The coefficient of compressibility, x, is calculated from the equation

$$x \cdot 10^{-7} = \frac{1}{v}\frac{dv}{dp} \text{ (kilograms per square centimeter)},$$

where v is the specific volume. As may be expected, the metals with the greatest atomic volumes, the alkali metals, are the most compressible, while those elements of low atomic volume, the transition elements and their near neighbors, are the least compressible. The value of the *linear* coefficient of compressibility (x_l) varies with the crystallographic direction. For example, Zn, which crystallizes in the hexagonal system, has a value of $x_l \cdot 10^{-7}$ equal to 12.96 (kilograms per square centimeter), parallel to the crystal axis, and $x_l \cdot 10^{-7}$ equal to 1.96 (kilograms per square centimeter) perpendicular to the crystal axis. There are many interesting polymorphic changes and accompanying changes in physical properties under high pressures, and the reader is referred especially to the work of P. W. Bridgman in this field.

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Melting Point.—The melting points of the metals follow the periodic grouping in the property tables. The metals with similar melting points are in the same groups. The low melting metals are, in general, convenient to cast but are of course not suitable

as a rule for high-temperature service. The melting points change with pressure, the direction of the change being determined by the volume change in the solid-to-liquid transition. If, as is usually the case, the volume increases on melting, an increase in pressure would tend to offset that change, and an increase in temperature would be necessary to cause melting. This is in accordance with the principle of LeChatelier. The increase in melting point, with increase in pressure, is illustrated in the case of tin by the phase diagram, Fig. 4, page 15. When the volume decreases on melting, an increase in pressure would tend to hasten that change, and the melting point would be lowered. This is the case for Bi, Sb, and Ga. The change in melting temperature, with increase in pressure, is more pronounced the greater the volume change on melting. Thus in ice skating, the pressure of the skate runner causes the ice to melt, forming a layer of lubricating liquid.

Thermal Expansion.—The change in dimensions of metals upon increase in temperature is measured linearly in centimeters per centimeter per degree, and the linear coefficient of expansion

$$\alpha = \frac{1}{l}\frac{dl}{dt}.$$

The maximum volume change of a solid body is about 6 per cent, as was shown by Gruneisen in the equation

$$\frac{V_m - V_0}{V_0} = 0.06$$

where V_m is the volume of the solid at the melting point and V_0 is the volume at absolute zero. The 6 per cent volume change is by no means regular in all metals, for polymorphic transformations result in discontinuous volume changes. Figure 45 shows the volume change of a hypothetical metal exhibiting polymorphic transitions upon temperature increase. The slope of the lines indicates the coefficient of expansion at any temperature and the departure from linearity indicates the change of the coefficient of expansion with temperature.

The change in volume, with change in temperature, accounts for the formation of piping during the solidification of an ingot, for shrinkage cracks in castings and welds, for quenching cracks in steel during drastic heating or cooling as in heat treatment,

and for checking or cracking due to grinding the surface of a metal on a high-speed wheel that heats the surface.

In single crystals of metals the linear expansion of the metal is an anisotropic property, the amounts of expansion being different in different directions through the crystal. The maximum variation in dimensional change in the hexagonal system is encountered in the direction either perpendicular or parallel to the principal crystal axis. For example, in Zn which crystallizes in the hexagonal system, $\alpha_{\parallel} \times 10^{-6}$ at temperatures from
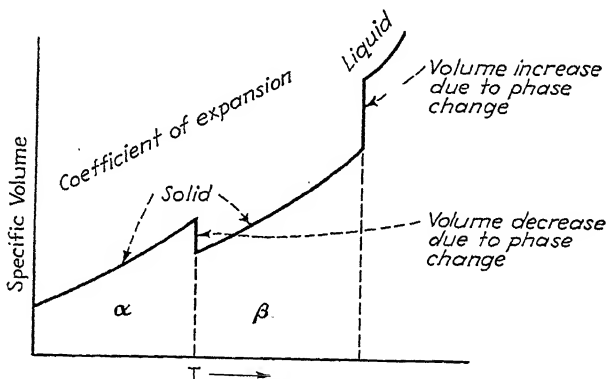
Fig. 45.—Schematic representation of the variation of specific volume with temperature through a polymorphic-phase change.

20–100°C. is 63.7 cm. per centimeter per degree, while $\alpha_{\perp} \times 10^{-6}$ is 14.1 cm. per centimeter per degree. The expansion of crystals upon heating may be understood in terms of the increased activity of the atoms as the temperature rises. The kinetic oscillations of the atoms increase in amplitude, and thus the average distance between atoms is greater, resulting in an expansion of the crystal lattices and of the entire mass.

Specific Heat.—The specific heat of a substance is defined as the amount of heat necessary to raise a unit mass of that substance one degree of temperature. It influences the rate at which liquid metal in a mold can cool and the rate at which heat may be abstracted from a forging during quenching. Figure 46 is a plot of heat content *vs.* temperature for iron. The slopes of the lines indicate the specific heat of iron, while the vertical lines indicate the change in heat content upon phase changes in iron up to the melting point.

The atomic heat of a metal is equal to its specific heat multiplied by its gram atomic weight. In 1819 Dulong and Petit found that at room temperature the atomic heats of all solid
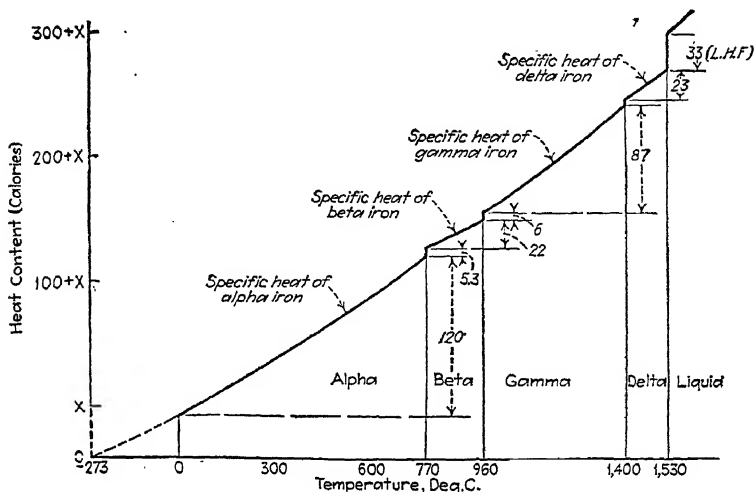
FIG. 46.—Heat content of iron.

elements were the same and equal to 6.4. The law is generally true, but there are notable exceptions, *e.g.*, carbon and boron exhibit low atomic heats at room temperature. A more general law, which may be applied to all solid elements, is that their atomic heats approach a constant value at high temperatures. Figure 47 is a plot of atomic heat *vs.* log T for Pb, Al, and C, which shows that the ultimate values for atomic heats are approximately the same, but that the attainment of that value is at different temperatures.

FIG. 47.—Variation of atomic heat with temperature. (*Courtesy of H. S. Taylor and D. Van Nostrand and Company, Inc.*)

The atomic heat may be calculated from specific heat measured at either constant pressure or constant volume, and the relationship between the two values is given by the equation

$$ c \quad c \quad \frac{TV\alpha^2}{ } $$

where T is the absolute temperature, V is the atomic volume, α is the thermal coefficient of expansion, x is the coefficient of compressibility, and k is a proportionality factor. The difference in the values has significance for only the elements with high coefficients of expansion, such as caesium, sodium, and potassium.

The specific heat of a metal determines the heat input and extraction necessary in heat-treating operations, the rate of cooling of liquid metal cast into a mold, the amount of time available for the escape of gases, etc.

The *characteristic temperature* of a metal, θ, is defined as that temperature at which the atomic heat of that metal is 5.49 cal. The value 5.49 cal. is so chosen that property measurements made at the characteristic temperature or equal fractions of that temperature tend to be made under corresponding conditions as regards atomic oscillation.

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Electrical Conductivity.—The most predominant electronic property of metals is electrical conductivity. It is of paramount importance in the telephone, radio, and electrical machine industries, and also in all electrical heating devices. The explanation of this property must be based on the concept of the metallic bond as presented in Chap. I. The substance of this concept is that the electrons are free to move throughout the lattice in definite energy levels while holding the positive atomic nuclei together. This freedom of movement of electrons provides a means by which a stream of electricity may be conducted through a crystal by the application of an external potential which accelerates the electrons and causes them to flow in the direction of the positive side of the applied potential.

Electrical resistance arises from any condition which tends to hinder this transfer and flow of electrons. Two important types of hindrance are recognized: (1) resistance inherent in the metal arising from (a) collisions of valence electrons with the oscillating

atomic nuclei and (*b*) from the extent to which the valence electrons are bound by adjacent atomic nuclei; (2) resistance arising from extraneous factors, such as (*a*) foreign atoms present as impurities and (*b*) internal stresses which distort and interrupt the energy levels at which electron transfer takes place.

Specific electrical conductivity σ_0, is expressed as the flow of current between two opposite sides of a cubic centimeter of metal at 0°C. and is calculated from Ohm's law $\sigma_0 = I/E$; where I is the current measured and E is the applied potential.

The reciprocal of the specific conductivity is the specific resistance ζ_0

$$\zeta_0 = \frac{1}{\sigma_0}$$

The specific resistance of pure metals at 0°C. is shown in the property tables.

For the purpose of comparing one metal with another, it is necessary to measure the conductivity of an equal number of atoms (atomic conductivity) either at their characteristic temperature θ or at some equal fraction of that temperature θ/T (see page 70). Otherwise, the crystal habit may play a larger role than do the atoms themselves. Atomic conductivity σ_{at} is calculated from the specific conductivity by the formula

$$\sigma_{at} = \sigma_{\frac{\theta}{T}} \sqrt[3]{\frac{A}{\delta}}$$

where A is the atomic weight, δ is the density, and $\sigma_{\frac{\theta}{T}}$ is the specific heat determined at a temperature of θ/T.

Examination of the property charts and the graph, Fig. 48 which is the atomic conductivity $\times 10^{-4}$ measured at $\theta°A$ plotted against the atomic number, shows that atomic conductivity generally increases within each periodic subgroup and that the univalent elements have the highest conductivity. This is to be expected from the fact that the larger the number of valence electrons, the more closely they are bound to the sharing nuclei and the less free they are for transfer. The comparatively high conductivities of trivalent Al and tetravalent Pb are explained on the basis that only a part of the valence electrons contributes to conductivity, *i.e.*, the metal in the solid state is only partially ionized.

Resistance increases with increase in temperature because of the effect of temperature on the resistance factors listed above (particularity 1 "*a*"). At high temperatures (above 100°A) R is proportional to T ($R \propto T = kT$). Figure 49 shows the effect
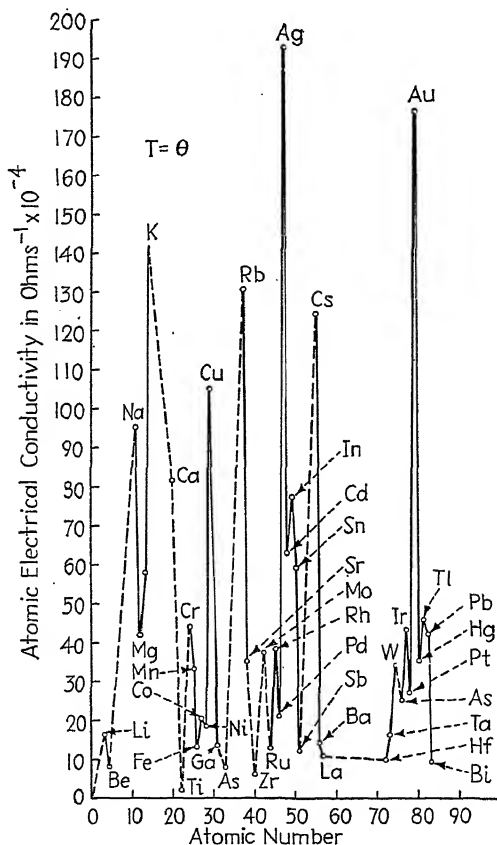
Fig. 48.—Periodic variation of atomic-electrical conductivity with atomic number. $T = \theta$.

of T at high temperatures for a number of pure metals. The nearly linear relationship of T to resistance in the solid state is the basis of the electrical resistance pyrometer.

Superconductivity.—As metals approach absolute zero, their resistance approaches zero. In some metals, however, the tendency is for resistance to approach zero at some finite temperature above absolute zero. Such metals are called superconductors.

Superconductivity cannot today be accounted for by theory. The application of small potentials to closed circuits of such
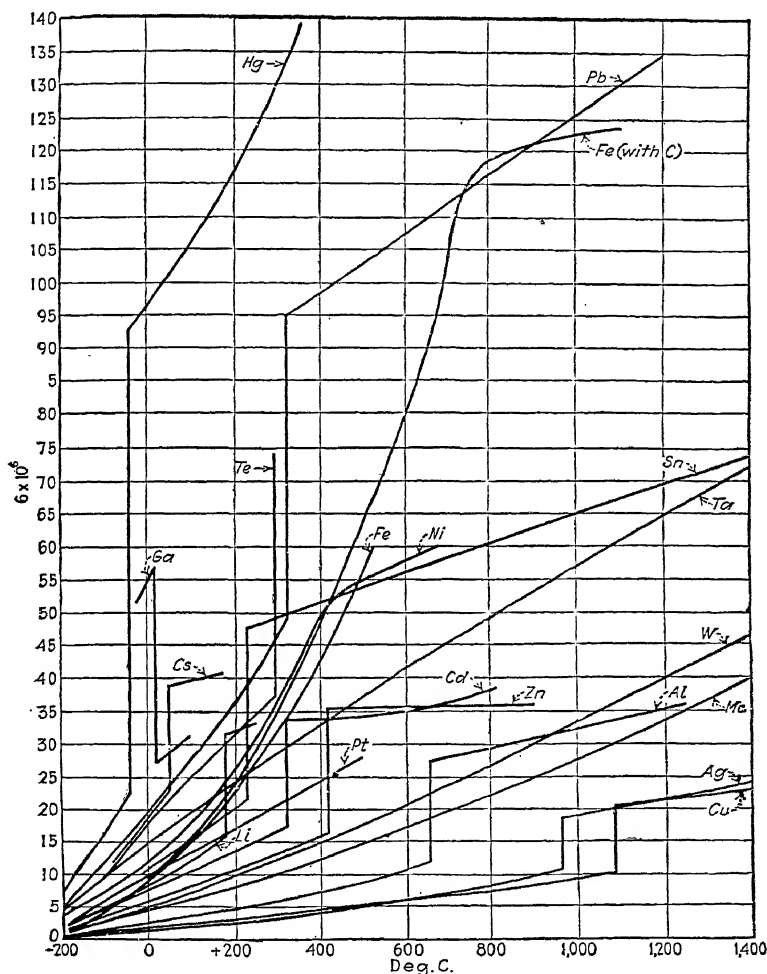
Fig. 49.—Electrical resistivity of metals at high and low temperatures. (*Guertler-Schulze.*)

metals is sufficient to cause current to flow indefinitely after the potential is removed.

Electrical conductivity is an anisotropic property in metallic single crystals.

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Heat Conductivity.—Another predominant electronic property closely allied to electrical conductivity is heat conductivity. In the case of heat conductivity, a temperature gradient or thermal potential is the exciting force, and the electrons are again the principal conducting agents. However, in heat conductivity the collisions of the vibrating nuclei add to the conductivity. At low temperatures this effect is negligible and conductivity is entirely due to valence electrons. The factors mentioned above which account for electrical resistance account also for resistance to heat conductivity.

The coefficient of heat conductivity, λ, is measured in calories per centimeter per degree per second, and the quantity of heat, W, passing through a body is then

$$W = \lambda A \frac{dt}{dx} t,$$

where A is the cross-sectional area, dt/dx is the temperature gradient, and t is the time. The atomic coefficient of heat conductivity, $\lambda_{at} = \lambda \sqrt[3]{A/\delta}$, where A is the atomic weight and δ is the density.

The data tables and the graph, Fig. 50, show the same general variation of values as were shown in electrical conductivity, but the anomalies due to partial ionization are more marked than in the case of electrical conductivity.

Thermal conductivity is an anisotropic property in single metallic crystals. The coefficient of heat conductivity is apparently independent of temperature within limits. Because of the great experimental difficulties in determining heat conductivities, comparatively little is known about the property. The thermal

conductivity of metals is of great practical importance in the refrigeration industry, in heating and ventilation, in heat interchangers and boilers, in the quenching and annealing of metals called *heat-treatment*, in internal-combustion engines, in welding, and in firearms.
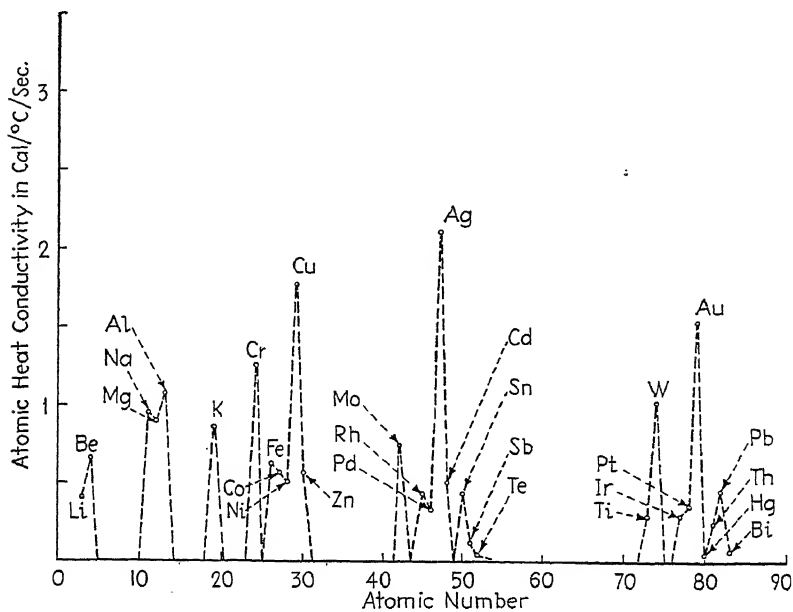
50.—The periodic variation of atomic-heat conductivity with atomic number.

An outstanding success of the electron theory is the prediction of the Wiedemann-Franz law relating heat and electrical conductivity on the basis of the electronic nature of the two properties. The law states that $\lambda/\sigma T = L = 2.4 \times 10^{-8}$ volt²/degree².

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Magnetism.—Metallic bodies, when placed within a magnetic field, may either concentrate or disperse the lines of force of that field, *i.e.*, they may have a magnetic field induced in them either

parallel to or in opposition to the applied field. Bodies of the former type are called *paramagnetic* and of the latter type, *diamagnetic*. An especially high capability of concentrating the lines of force of the applied field is exhibited by the metals Fe, Co, and Ni. These are known as *ferromagnetic* metals. Alloys of these metals with each other and with some of the other elements, along with a few alloys made up of nonferromagnetic metals, exhibit the property of ferromagnetism. The alloys will be treated in a later chapter.

The elementary magnetic particle is the spinning electron, which, spinning on its own axis, acts as a small gyroscope. Thus
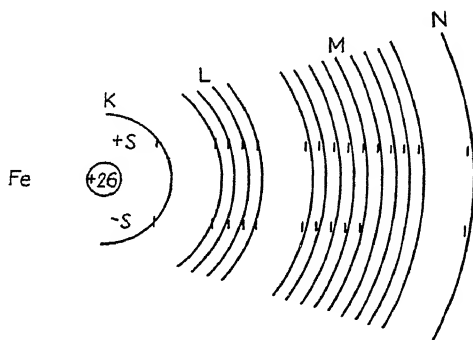
Fig. 51.—Electron shells in the iron atom.

the electron possesses a definite magnetic moment because of its moving electrical charge. When a magnetic field is applied to the electrons of an atom, it tends to align the spins parallel to the applied field. As will be remembered from Chap. I, Pauli's principle states that no more than two electrons of opposite spin may occupy any one energy level. Consequently, in full energy levels, the magnetic moment of each electron would be balanced by the other when the electrons are aligned parallel but are spinning in opposite directions. However, where the energy level has only one electron there is an unbalanced magnetic moment present. Such a magnetic moment is a necessary, but not a sufficient, condition for ferromagnetism. Figure 51 shows the accepted electronic configuration for Fe. Fe has four excess electron spins, Co has 3, and Ni has 2. However, nonferromagnetic metals—Mn, Cr, and many others—have unbalanced electron spins, but they are not ferromagnetic.

The other necessary condition that results in ferromagnetism arises from what are termed *exchange forces*, which act to keep electron spins parallel. They are difficult to describe because of the difficult concepts of wave mechanics involved, but it may suffice to say that the exchange forces tending to keep the spins aligned are opposed by thermal vibrations, which tend to destroy the spin alignment. When the exchange forces predominate, the body is ferromagnetic.

In the ferromagnetic metals, the large forces of exchange result in parallel spin alignment, even when no magnetic field is

DEMAGNETIZED

CRYSTAL AXES

SATURATED
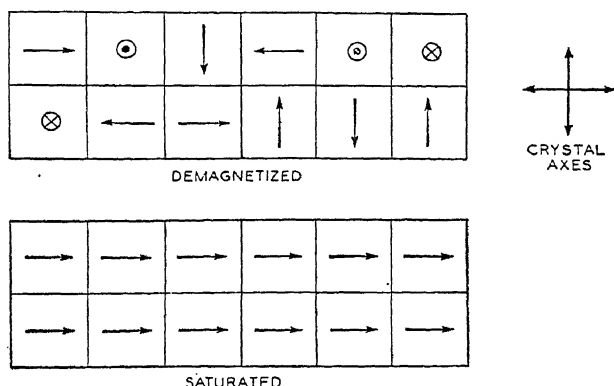
FIG. 52.—Schematic illustration of magnetic domains in a single crystal of iron. (*Courtesy of Dr. R. M. Bozorth and the American Institute of Electrical Engineers.*)

applied. Such alignment is limited to small elemental cubes of the order of 0.001 in. on an edge called *domains*. In the absence of an applied magnetic field, these domains oppose each other statistically and the total macroscopic magnetization of the piece is zero. Upon the application of an external field, these domains snap over into alignment with each other and an induced field results (see Fig. 52).

Even though the snapping over of the individual domains cannot be measured by any instrument that we now have at our disposal, it may be demonstrated by connecting a coil wrapped about the specimen to be magnetized with an amplifier and earphones. The actual snapping over of the domains upon slow increase in the intensity of the field can be heard as a series of clicks. The resulting magnetization curve should thus be a series of steps, as indicated in the enlarged portion of Fig. 53a.

The magnetization in discrete steps is known as the *Barkhausen* effect. The greater the strength of the applied field, the more domains swing into alignment, until they are all aligned at saturation.
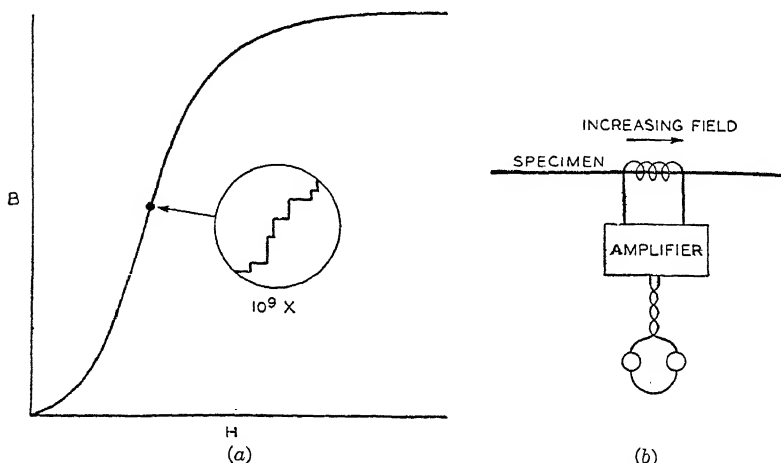
FIG. 53.—Diagram of curves obtained and equipment used in investigating the Barkhausen effect. (*Courtesy of Dr. R. M. Bozorth and the American Institute of Electrical Engineers.*)

The fact that the exchange forces are opposed by thermal agitation results in a continual decrease of the saturation value of magnetization as temperature increases until at some tempera-
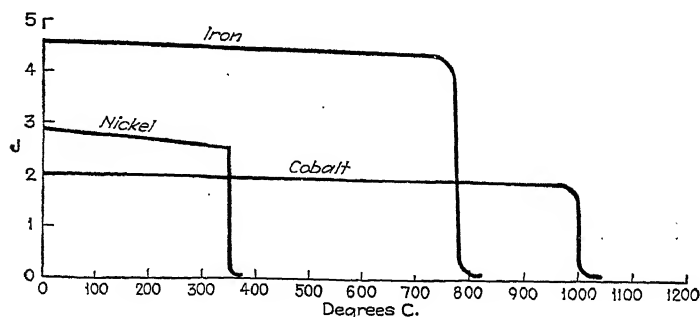
FIG. 54.—Loss of ferromagnetism with rise in temperature. (*Tammann.*)

ture known as the *Curie temperature*, agitation overcomes exchange forces, ferromagnetism disappears, and a strongly temperature-dependent paramagnetism replaces it. Figure 54

shows the loss of ferromagnetism with rise in temperature for Fe, Co, and Ni.

Ferromagnetism is an anisotropic property, *i.e.*, the electron spin is aligned parallel to one direction within the space lattice more easily than to others. In Fe, the [100] direction is the direction of easiest magnetization, while in Ni it is the [111] direction, as shown in Fig. 55. The [1,000] direction, or the direction parallel to the principal axis in cobalt, is the direction
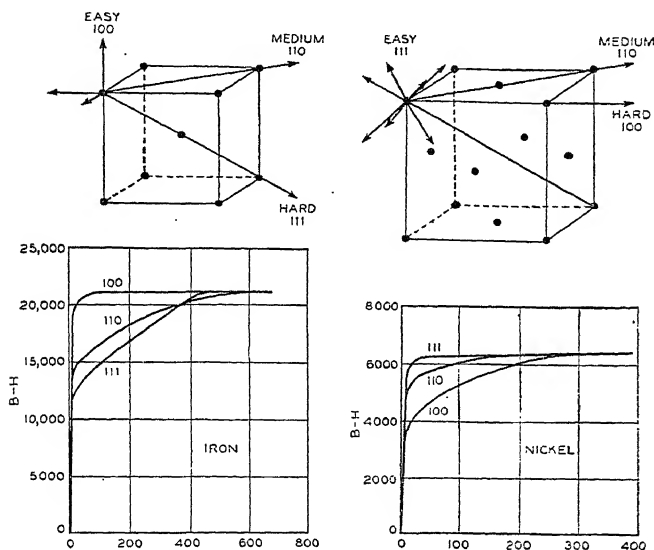
FIG. 55.—Magnetic properties and crystal structures of single crystals of iron and nickel (*Beck, Honda and Kaya, Webster*). (*Courtesy of the American Institute of Electrical Engineers.*)

of spin alignment. In Fe there are six mutually perpendicular [100] directions; in Ni, 8 mutually perpendicular [111] directions; and in Co there are 2 opposite [1,000] directions.

Before the application of an external field, each domain is aligned parallel to one of the directions of easiest magnetization. If the field is applied parallel to one of these directions, saturation is comparatively easily reached. If, however, the applied field is not parallel to one of these directions, saturation is reached in two different steps. The first is the snapping over of the domains parallel to the direction of easiest magnetization nearest to the applied field, and then the actual rotation of these

domains into the direction of the applied field with further external excitation, as shown in Fig. 56.

Magnetization results in an actual change in length of the magnetized piece called *magnetostriction*. Consequently, stresses or strains present during magnetization greatly influence the ease with which a body may be magnetized, depending upon

DEMAGNETIZED

CRYSTAL AXES

SUDDEN REVERSALS COMPLETE
(KNEE OF MAGNETIZATION CURVE)

MAGNETIC FIELD

SATURATED, DOMAINS ROTATED
IN HIGH FIELD
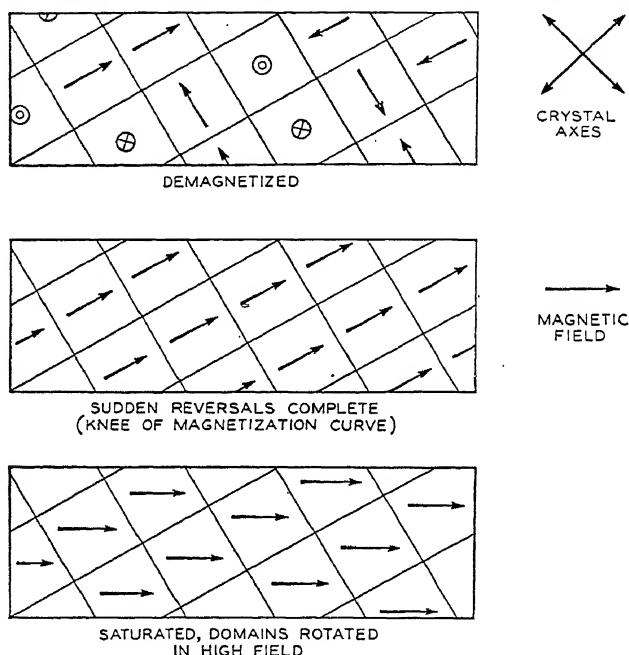
FIG. 56.—As the magnetic-field strength increases, domains first change direction suddenly, then rotate smoothly. (*Courtesy of Dr. Bozorth and the American Institute of Electrical Engineers.*)

whether or not the stresses or strains aid or oppose the deformation resulting from magnetostriction.

Upon the removal of the applied field, all the domains do not necessarily return to their original position. They may be held in position by lattice distortion. Those domains that remain in the magnetized condition contribute to a residual magnetism known as *remanence*. The magnetic field that must be applied in the opposite direction to remove that remanence is known as the *coercive force*. It now becomes easy to see why hardened steels that contain much lattice distortion, and thereby prohibit the return of domains to their original positions, make the best

permanent magnets. Since most of the industrially important magnetic materials are alloys, rather than pure metals, these practical examples will be considered later in the book.

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Thermoelectricity.—If two homogeneous metallic wires, of compositions a and b, are connected in a circuit, and the two junctions are maintained at different temperatures, a current will flow in the circuit and it may be measured by a galvanometer suitably inserted in the circuit (Fig. 57). The current thus produced is called a *thermoelectric* current and the circuit that produces it, a *thermocouple*. The couple is the agent that results in an E.M.F. that produces the current. The effect was first stated by Seebeck and is known as the *Seebeck effect*. The regular variation of this potential with temperature, for certain pairs of metals, accounts for its use in the measurement of temperature by the familiar thermocouple. The law of Magnus, as modified by more recent considerations, states that in a thermocouple composed of a homogeneous metal, the total E.M.F. depends only on the temperature difference of the

FIG. 57.—Thermoelectric circuit produced by wires a and b through a galvanometer.

two junctions and not on the way in which it is distributed between them. The thermoelectric properties are primarily electron functions and the thermoelectric energy relationships may be exactly accounted for by thermodynamics. The electrons in the two metals composing a thermocouple will not be under the same pressure, *i.e.*, they will not have the same energy, and when the two are placed in contact, there is a flow of electrons from one metal to the other. In this way a potential difference will be set up

between the two metals, due to the gain of electrons by one and the loss of electrons from the other. When the two junctions of the couple are at the same temperature, the effect at one balances the effect at the other, but with a difference in temperature, an actual current flows as a result of the difference in electron transfer at the junctions.

The *Peltier* effect is the phenomenon of heat evolution or absorption at the junction of two dissimilar metals when a current is passed through the junction. The resulting Peltier heat is positive if a positive current flowing from one metal to the other causes the evolution of heat at the junction, and negative if it causes the absorption of heat at the junction. Reversing the direction of the current reverses the heat effect. The Peltier heat arises from the work that must be done on, or is done by, the electrons in the transfer across the boundary. The possibility is suggested, for example, that the cutting tip of a lathe tool might be cooled during machining by passing an electric current through the tool and the object being machined.

The *Thomson* effect is that effect which results in the redistribution of heat in a homogeneous wire containing a temperature gradient when a current flows along it. In order to maintain the original temperature distribution, heat must be artificially added to or abstracted from the wire.

Summary.—Thus the properties known as *density, atomic volume, compressibility, melting point, thermal expansion, specific heat, electrical* and *heat conductivity, magnetism,* and *thermoelectricity* have been briefly reviewed in the light of our present knowledge of atomic structure and crystal structure. Their relationships through the periodic table have been pointed out and a few of their important industrial applications have been referred to. In this field the physicists are making increasingly important contributions. While these studies have been concerned entirely with pure metals, rather than with the industrially more important alloys, they reveal, nevertheless, the basic phenomena underlying metallic properties. As we shall see later, they apply equally to alloys. They are the fundamental concepts of metallic behavior.

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CHAPTER III

THE MECHANICAL PROPERTIES OF METALS. THEIR CHANGE WITH TEMPERATURE

THE DEFORMATION OF A METAL

Elastic Deformation.—If a metal is stressed very slightly, a temporary deformation of the metallic crystallites takes place, permitted apparently by an elastic displacement of the atoms in the space lattices. Removal of the stress results in a gradual return of the object to its original dimensions. Because a part of the recovery is gradual and asymptotic to the time axis, a given piece of metal at a given time may retain in it traces of all the deformations that it has received prior to that time, although they may be small in magnitude and constantly diminishing. The conditions in this region are expressed approximately by Hooke's law, which says in case of the tension test[1] that deformation e is proportional to applied stress: $\left(e = \dfrac{P}{A} \dfrac{L}{E} \right)$. P is the force in pounds; A is the area of the section in square inches; L is the original length; E is the modulus of elasticity; and e is the elongation produced by the tension. Thus, service stresses in a metallic structure, being below the elastic limit, usually produce deformation in accordance with the modulus of elasticity E of the metal and entirely independent of its tensile strength and plasticity. This fact is not always appreciated in the design of structures or in the specification of physical properties of materials of construction. It is important to note also that as the speed of test varies, the elastic limit varies, the limit decreasing as the rate of stress application decreases. It is important, further, to note that the more sensitive the measuring methods are, the lower will be the values obtained as the elastic limit of the material. There seems thus to be no intrinsic elastic limit for the ordinary metallic material. However, present industrially accepted tests do measure an empirical

[1] The tension test is discussed on pp. 323 *ff.*

84.

elastic limit and this limit is utilized in the design of metal structures.

Plastic Deformation.—If the metal is stressed far beyond the elastic range, it will never return to its original form. Plastic deformation, or *flow* of the metal under the force has taken place.

The plastic flow of metals is perhaps their most important behavior, the one that distinguishes them most sharply from other materials of construction. Some of the most important metallurgical operations known as *shaping* are in fact essentially examples of plastic deformation. For instance, the stamping of automobile parts, pressing of large objects, spinning of aluminum pans, rolling of boiler plate, rails and I-beams, drawing of wire, extrusion of moldings or telephone cable, and forging of shafts are all processes involving the plastic deformation of the metal. Riveting and bending are similar processes. Included also are the various machining operations, such as milling, turning in a lathe, sawing and punching, as of rivet holes. Clearly these operations extend throughout many of our most important industrial processes, and the behavior of the metal under this treatment must be of essential interest in perfecting the operation.[1] The changes produced in the properties of the metal so deformed are important also. We shall consider first the deformation of metal while cold, called *cold working*.

The Deformation of a Single Crystal.—The study of the mechanism of the deformation that takes place in each crystallite of a cold-worked metallic object can be simplified by singling out one single crystal and observing how it behaves under similar deformation. Many of the important mechanical properties of a metal are to be understood from the behavior of the single crystals of which it is composed. The preparation of a single crystal wire was described on page 38. After we have examined the behavior of a single crystal under deformation we shall then come to the study of an ordinary crystalline aggregate or metallic object with a clearer view.

Deformation by Slip.[2]—If stressed in tension a single crystal of zinc elongates slightly, a line appears around it showing dis-

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[1] Some of the more interesting methods of shaping metals industrially are illustrated on pp. 290 and 291.

[2] The actual case of the deformation of a single crystal is not so simple as here presented. Rather than there being individual displacements occurring

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placement of one part of the wire with respect to the other, and elongation stops. If the stress is raised, another line parallel to the first appears indicating another displacement and again slip stops. Each successive extension requires a *higher stress* and is accompanied by the appearance of another slip line, which
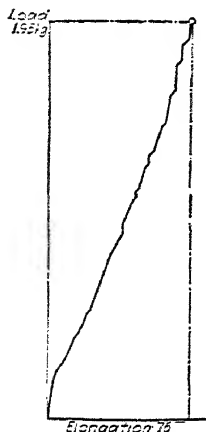
Fig. 58.—Stress-strain diagram of a zinc single crystal.

is actually the intersection of a slip *plane* through the crystal with the surface of the wire. The slip planes are found to be parallel to the basal plane of the hexagonal zinc crystal. Figure 58 shows the stress-strain diagram for such a crystal with the gradual rise of stress and the constant amount of elongation per movement, and Fig. 59 shows the appearance of the surface of the specimen after a great many movements have taken place. It resembles that of a pack of cards which has been pushed lengthwise. The wire, originally cylindrical, has become ribbon shaped. Finally it breaks, the fracture at low temperature, being parallel to the slip planes. The tensile strength is only about one-tenth that of a similar specimen of commercial zinc.

Polanyi has constructed a model, Fig. 60a, in which he shows the slip planes parallel to the base of the hexagon for a zinc single crystal. Figure 60b shows the slip of fragments of the crystal parallel to this basal (0001) plane. This is the plane of densest atomic population in zinc. The inclination of this plane to the axis of the single crystal wire at the beginning of the test depended upon chance during the growth of the wire from the melt. As slip continues, this plane tends to become parallel with the axis of tension as shown in Fig. 60c.

By examination of the orientation of the slip planes with respect to the applied stress, it is found that slip has taken place through the action of a simple shearing stress. This stress is the component of the applied stress which is parallel to the slip plane. Upon increasing the original angle between the slip plane and the applied stress, we find a higher absolute stress, but the same

successively in the crystal during deformation, it is more likely that many such displacements evidenced by many glide elipses appear simultaneously in the crystal at the early deformation stages.

resolved shear stress is necessary to produce the first slip in every case. This fact is clearly brought out by the examination of the graphs of stress *vs.* strain, expressed ordinarily as elongation, and resolved shear stress *vs.* strain, expressed as crystallographic shear, for the same set of orientations, shown in Figs. 61*a* and *b*.
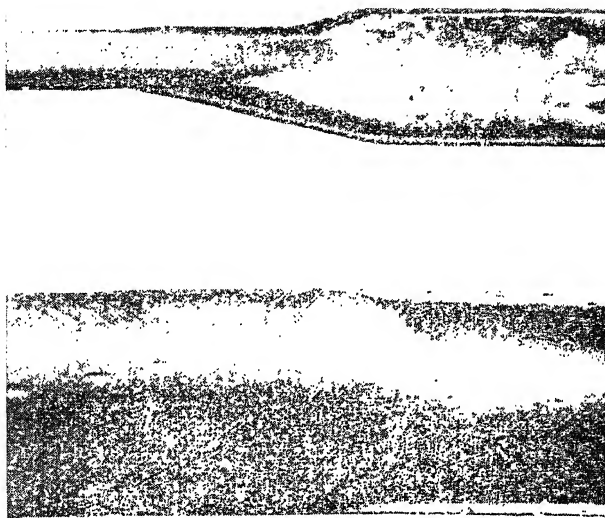
Fig. 59.—Appearance (side and top views) of an elongated zinc single crystal. Note effects of polycrystalline region at right end. (*Courtesy of Mr. R. F. Miller.*)

The *direction* of slip on this plane is not the direction of greatest stress, shown by the long arrow in Fig. 60, but is one of three directions parallel to the three pairs of parallel sides of the hexagon, namely, the one direction *nearest* to that of the maximum-stress arrow. This direction is one of the three *directions* of densest atomic population in the zinc crystal. As slip proceeds, this direction gradually becomes parallel with the tension axis. Hence we may say that both the plane of slip and the direction of slip tend to rotate into the axis of tension as deformation proceeds. The combination of a slip plane and a slip

direction is known as a slip system. There are, consequently, three slip systems in a hexagonal crystal. If the slip system had (by chance) been at right angles to the tension axis in the beginning, or at such an angle that the component of stress parallel to the plane of slip were too small to produce slip, then fracture would take place without slip. The dependence of orientation of the basal plane with respect to the tension axis upon the
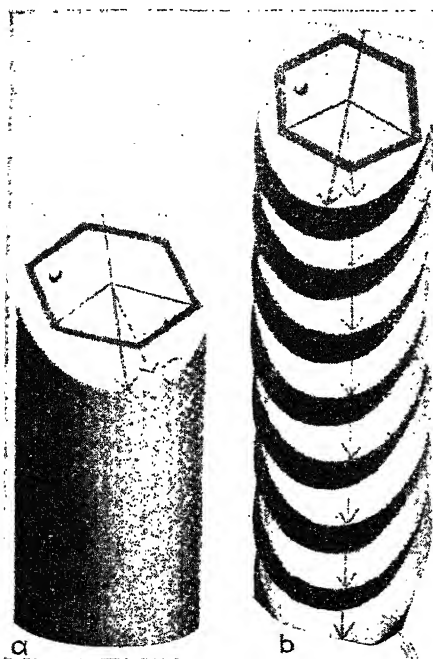
Fig. 60.—Model of a zinc single crystal. (*a*) Undeformed; (*b*) deformed, front view; (*c*) deformed, side view. (*Mark, Polanyi, and Schmid.*)

elongation of a magnesium (also hexagonal) single crystal, is shown in Fig. 62. It will be observed in Fig. 60 that the sliding blocks move as units. Furthermore, X-ray evidence shows that the lattice structure of the deformed crystal, although the crystal is shattered and distorted, is preserved. Therefore slip can be tentatively defined as the relative movement of the sliding blocks with respect to each other, of one lattice dimension or a multiple of that dimension in the slip direction. This simplified picture of the slip mechanism does not include certain complicating phenomena which have been observed.
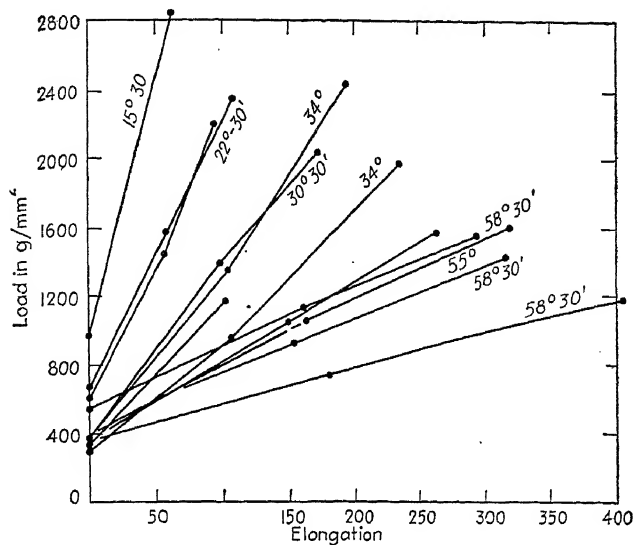
FIG. 61(a).—Stress-strain diagram for Zn crystals with their basal planes oriented at various angles to the applied stress. (*E. Schmid and W. Boas.*)
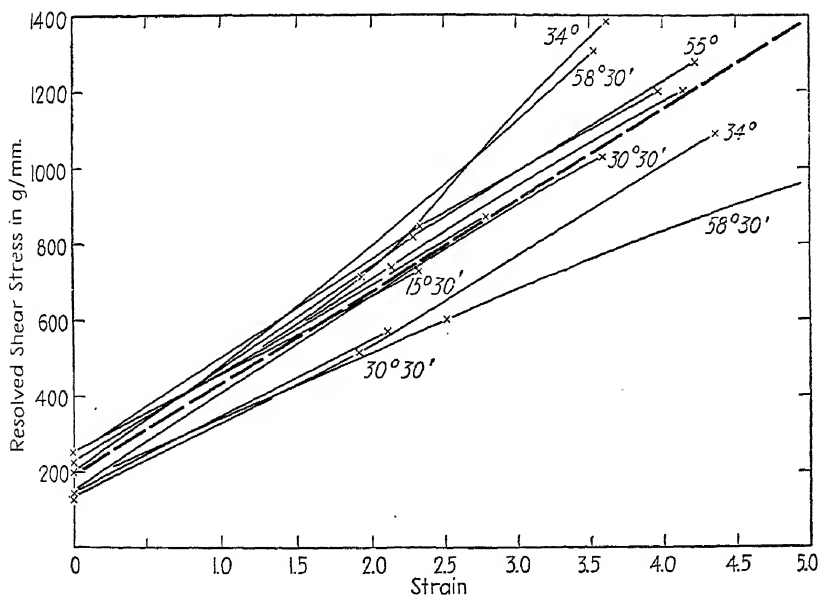
FIG. 61(b).—Resolved shear stress *vs.* strain of zinc crystals with their basal planes oriented at different angles to the applied stress. (*E. Schmid and W. Boas.*)

Slip versus Crystal Structure.—Because of the anticipated simplicity of the slip processes in the hexagonal system, the basal plan only being active, zinc was chosen for the above illustration.

However, in the cubic system, the slip process is not so simple. Experience has shown that deformation generally proceeds on the most densely populated planes in the crystal system, presumably because those planes are the strongest. The distances between these planes are often the maximum interplanar distances also. The direction of slip on those planes is always the direction of greatest linear population in the planes. In the face-centered cubic system, the {111} family of planes is the most densely populated and there are four groups of planes whose intercepts are {111}.
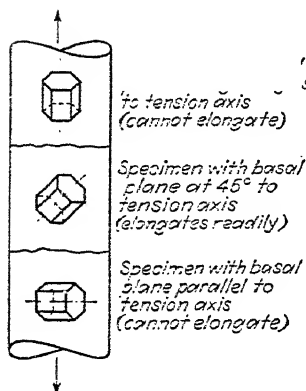
FIG. 62.—Yield points of magnesium crystals of various orientations. (*Schmidt in Metals and Alloys, July,* 1934.)
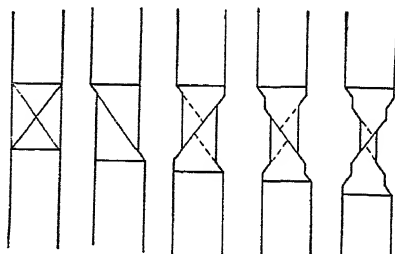
FIG. 63.—Schematic picture of gliding along two glide planes. (*After Smithell's.*)

In each of those planes there are three directions of maximum density, namely the [110] directions. Hence the face-centered cubic system has 12 possible slip systems. The same principles of slip again apply, slip taking place within those slip systems upon which the resolved shear stress is the greatest in both plane and direction, as determined by orientation of the crystal with respect to the applied stress. The rotation of both the plane and direction of slip into the axis of tension proceeds just as before.

The availability of a large number of slip systems presents the possibility, however, of having more than one plane oriented favorably for slip at the same time. Such a condition does not alter the principle in the least; we now have what is known as *double translation,* or *slip,* each plane operating alternately, as indicated in Fig. 63.

Lines caused by the intersection of double slip planes on the surface of a single crystal of Al are shown in Fig. 64.

Where so many slip systems are available, we should expect metals crystallizing in the cubic system, such as, for instance,

Fig. 64.—Double slip in aluminum single crystals. (*E. Schmid and W. Boas.*)

Fe, Cu, Au, and Al, to be much more plastic than those crystallizing in the hexagonal system, as Zn, Cd, and Mg.

The body-centered cubic system is the most complicated system of all, for here specific cases provide exceptions to the general rule, and slip does not always follow the {110} planes, the planes of densest atomic population. Alpha iron is one of these exceptions and there are enough possibilities of slip plane and direction
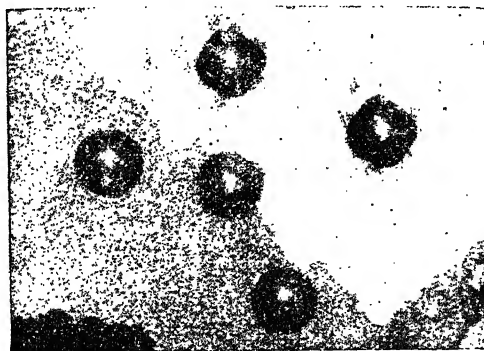
Fig. 65.—Ball impressions in iron; above: in a single crystal; below: in polycrystalline material. (*Czochralski.*)

combinations to present 48 possible slip systems in iron. The greater tendency to slip in certain planes of an iron single crystal is well illustrated in Fig. 65. A small ball was pressed into the surface of an iron single crystal, with the result that a four-cornered impression was produced, owing to the lower flow pressure at each corner as compared with that at 45 degrees to the corners. In the polycrystalline part of the specimen the impres-

sions are truly spherical due to the fine grain size and random orientation of the grains.

TABLE IV.—SLIP AND RUPTURE STRESSES FOR SINGLE CRYSTALS ON THEIR PRINCIPAL PLANES OF SLIP (*Sauerwald*)

Metal	Temperature, °C.	Slip stress, g./sq. mm.	Rupture stress, g./sq. mm.
Zn	−185	126	180
	20	36	
Bi	− 80	>625	324
	20	221	324
Al	200 to F. P.	101	
	20	300	

Temperature.—The resistance to slip in a single crystal increases rapidly as the temperature falls as shown in Table IV for Zn, Bi, and Al.
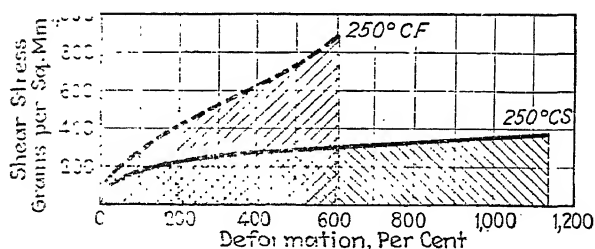
FIG. 66.—Stress-strain diagram of magnesium single crystal at 250° C. The velocity of deformation *F* is 100 times that of *S*.

Rate.—The slower the rate of deformation, the greater the deformation achievable without fracture and the lower the stress that must be applied, as shown in Fig. 66 for magnesium single crystals. The rate *F* is one hundred times faster than that marked *S*. Although the work done (area under the curves) is the same in each case, the elongation of specimen *S* is nearly double that of *F*. This relation holds also for temperatures other than 250°C.

Aspects of Slip.—As a summary, then, slip consists of a simultaneous rotation of the slip plane and direction into the direction of the applied stress through the action of a resolved shear stress.

The slip is accompanied by a continued rise in the magnitude of stress required for continued deformation. Slip differs from the simple gliding of two plates over each other, in that (1) its extent is limited to an interatomic distance or a multiple of that distance; (2) its plane and direction are determined by internal
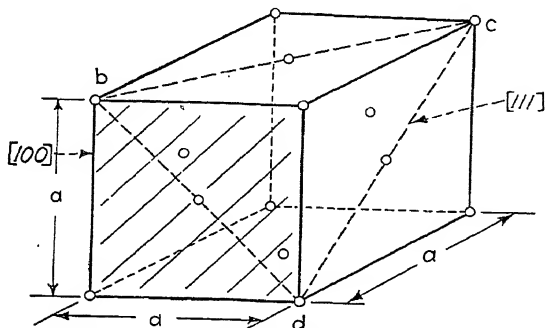
Fig. 67.—Schematic diagram of the slip plane in a face-centered cubic lattice.

directional forces; (3) the frictional resistance of gliding does not increase as gliding proceeds, while resistance to slip does; and (4) the energy of gliding is entirely dissipated by heat, while part of the energy of slip is stored up within the crystal as potential energy. Slip is diagrammatically illustrated in Figs. 67 and 68 for face-centered cubic elements. The (111) plane *bcd* in Fig. 67
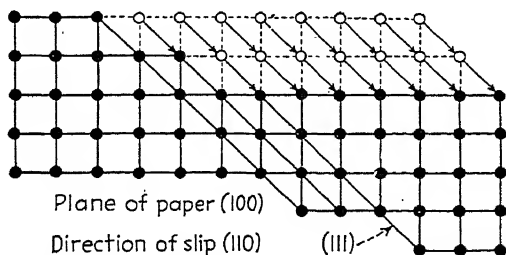
Fig. 68.—Schematic diagram of slip plane and direction in a cubic lattice.

is the plane of densest atomic population and is the plane along which slip occurs. It can be seen that the (111) plane intersects the (100) plane in the line *bd*. When the (100) plane is taken as the plane of the paper and several unit cells are grouped together, as in Fig. 68, slip is seen to be block movement along the (111) planes in a [110] direction a distance of one lattice dimension, or a multiple of that dimension.

Bending in single crystals of Zn is diagrammatically illustrated in Fig. 69. Bending must occur, otherwise the zinc crystal shown at *a* would, after elongation, appear as at *b*. Actually it appears as at *c*, with the bending illustrated at III. Figure 70 shows bent slip layers in a Sn single-crystal-tension specimen.
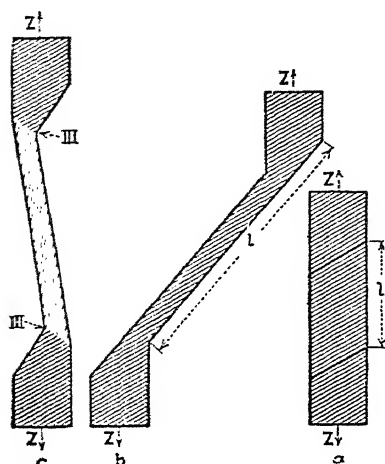
FIG. 69.—Bending of slip planes in a zinc single crystal. *(Polanyi.)*

The most remarkable feature of the deformation of a metallic crystal is the self-stopping of slip once started and the ability of the adjacent fragments to cling to each other instead of separating as in fracture. The plasticity of crystalline material thus depends upon its ability to form slip planes. If it cannot do so, it will be brittle.

Another remarkable feature is that the stress required to produce slip on the first plane is lower than that required for subsequent planes. In other words, work hardening is general throughout the specimen and is not limited to the operative slip plane.

FIG. 70.—Bent slip layers in a tin single-crystal tension specimen. Note the transition from wire (at left) to ribbon, the *edge* of which is at the right. *(Polanyi.)*

Deformation by Twinning.—Certain crystals may also deform by twinning, a mechanism by means of which a portion of a crystal may change lattice orientation with respect to the rest of the crystal. The twinned section may participate in deformation in two ways: (1) The twinning itself may accomplish an extensive change in shape, and (2) it may also facilitate further slip by placing the planes of potential slip into more favorable

positions with respect to the applied stress. Thus twinning is a second important method by which crystalline bodies may change their shapes. The mechanism of twinning (Schmid and Boas) may be described as the simple sliding of one plane of atoms over the next, *the extent of the movement of each plane being proportional to its distance from the twinning plane.* Figures 71 and 72 illustrate twinning in the face-centered cubic system. The (111) plane is the plane of densest atomic population and is the twinning plane *bcde* in Fig. 71. The shaded plane is the (110) plane, and is intersected by the (111) plane at the line *ce*. If the (110) plane lies in the plane of the paper and several cells are taken together, the twin mechanism is as

Fig. 71.—Twinning plane (*111*) in the face-centered cubic lattice.

shown in Fig. 72. The twinning plane is the (111) plane containing the direction *MN*. Each (111) plane in the twin section is operative in shear along the designated direction, and the first one, *UV*, moves one-third of an interatomic distance; the second,
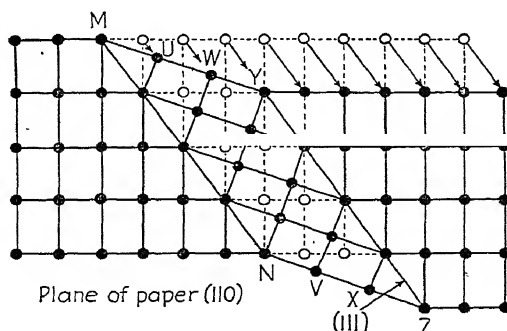
Fig. 72.—Schematic diagram of twinning in a cubic lattice.

WX, moves two-thirds of an interatomic distance; and the third, *YZ*, moves an entire spacing. The resultant crystal sections are mirror images of each other.

Figure 73 illustrates twinning in a calcite crystal. A wedge was driven down into the cleavage plane of the calcite, and the

section to the right of the wedge was shoved over like a deck of cards along the twinning planes. Figure 74 shows a wooden model illustrating what has happened. Figure 75 shows twin markings in single crystals of zinc, cadmium, and bismuth.

Fig. 73.—Twinning in a calcite crystal along the cleavage plane. (*E. Schmid and W. Boas.*)

Schmid and Wasserman have shown an interesting example of the facilitation of slip in a single crystal zinc wire by twinning. They found that when the basal (1000) plane or slip plane was oriented at small angles to the tension axis, owing to rotation induced by slip (see Fig. 60), there was a sudden necking or thinning of the wire, which led to further deformation and frac-
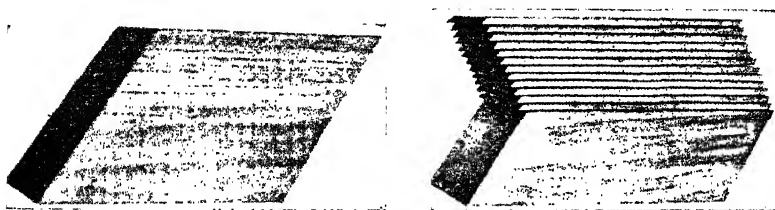
Fig. 74.—Schematic illustration of twinning by means of a wooden model. (*After Mügge.*)

ture. In the necked region slip bands appeared at 90 deg. to the original basal plane. X-ray examination proved them to be the basal (1000) planes within a twinned portion of the crystal.

Summary.—Thus it is clear that the deformation of a metallic crystal takes place by slipping, bending, and rotation, or by twinning of crystal fragments, or by a combination of all four processes. Slip usually takes place most readily parallel to the

planes of densest atomic population and in the direction of densest atomic population on these planes, although these conditions may change with the temperature. For this reason, probably, those crystals having the largest number of planes of dense atomic population, as for example the face-centered cubic, have the greatest formability, because they possess a large number of planes and directions of easy slip. The stress required

FIG. 75.—Twin markings on Zn, Cd, and Bi single crystals. (*E. Schmid and W. Boas.*)

to cause the first slip is the elastic limit or destruction limit of the crystal. It is a definite quantity for each metal, but varies with the temperature. Frictional resistance to slip increases as slipping continues until finally the stress rises far enough to produce slip in a new plane. Bending of the slip planes occurs during deformation and rotation of the crystal fragments to bring the slip planes and slip directions more nearly parallel to the direction of stress. Single crystals are quite weak as compared with ordinary metallic objects.

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Deformation of Polycrystalline Material.—The simplest transition from single-crystal to polycrystalline deformation is by the consideration of very coarse-grained materials. Figure 76 shows

Fig. 76.—Coarse-grained tungsten bar, showing obstructed deformation at grain boundaries. (*Smithells.*)

the effect of grain boundaries upon deformation in a coarse-grained tungsten material. Deformation has taken place outside the grain boundaries, the grains deforming according to their crystallographic laws. Those grains most favorably situated for deformation with respect to the applied stress deformed first, and after work hardening in those grains, deformation took place in less favorably oriented grains, but in no case did deformation proceed across the grain boundaries. Hence, the change in orientation from one grain to the next resulted in increased resistance to deformation at that point. In this illustration, deformation conditions closely resembled those in single crystals because, except at the junctions of two neighbors, the individual grains were free to deform according to crystallographic laws.

Single crystals and polycrystalline aggregates as coarse as the one just considered are the exception rather than the rule. Normally all crystals, except those at the surface, are completely surrounded by differently oriented adjacent crystals; their deformation must be transmitted through the grain boundaries, and their individual changes in shape must conform to the change in shape of their neighbors. Immediately we see the strengthening effect of polycrystallinity and can infer that decreased crystal size for a given volume would increase the strength and hardness of the piece. Moreover, we saw in the study of single crystals that deformation conformed to certain crystallographic laws, *i.e.*, slip took place on certain planes in definite directions.

Deformation in polycrystalline aggregates must also conform to the same crystallographic laws, but we can see that as deformation proceeds, many more slip systems may have to operate, owing to the restrictions encountered on the most favorably oriented systems. Such a condition is easy to meet in cubic metals, where there are many possible slip systems; but in hexagonal metals, where there are relatively few systems, it is more difficult to attain and indeed we find that hexagonal metals
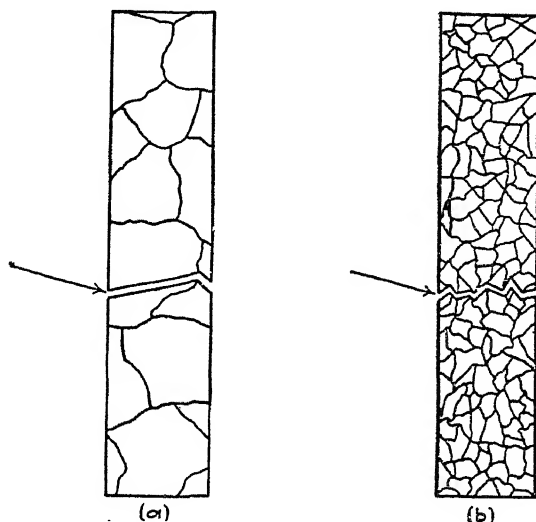
Fig. 77.—(*a*) Brittleness of coarse-grained metal under shock; (*b*) frequent change of direction of force in rupture of fine-grained metal.

under ordinary conditions reveal far less extensive deformation characteristics than do cubic metals.

In general, then, the more crystallites there are in a unit volume (finer grain size), the harder and stronger the material will be. Its resistance to shock, *i.e.*, to a suddenly applied force, is also improved.

The effect of grain size on impact is shown clearly in Fig. 77*a* and 77*b*. Only that component of force parallel to the operative slip plane in each grain is effective; and the smaller the grain size, the more often the change in slip direction.

The effect of grain size on tensile strength is clearly shown by the work of Edwards and Pfeil. Some of their results are reproduced in Fig. 78, in which stress is plotted *vs.* elongation for

various grain sizes in iron.   In specimens 1, 2, and 3 the average diameters of the crystals were 9.7, 7.0, and 2.5 mm., respectively.
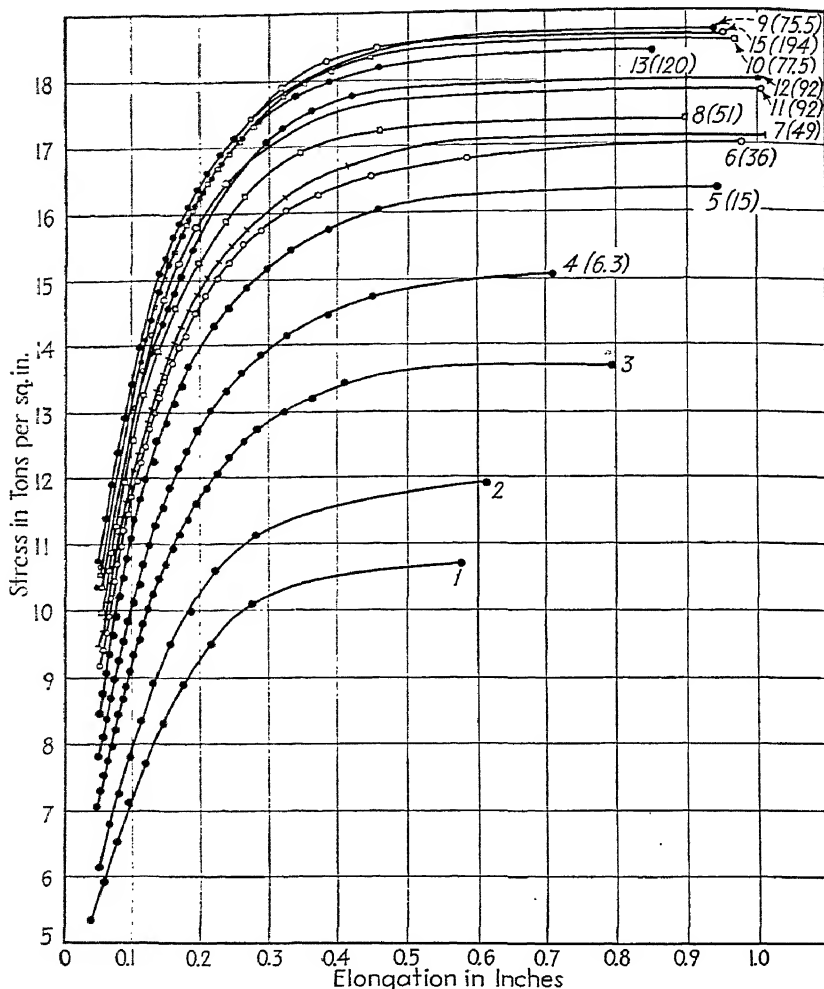
Fig. 78.—Stress-elongation curves for iron.   The numbers in parentheses following the specimen number gives the number of grains per square millimeter. Specimens numbered 1, 2, and 3 had grain diameters of 9.7, 7.0 and 2.5 mm., respectively.   (*Courtesy of C. A. Edwards and L. B. Pfeil, Journal of the Iron and Steel Institute.*)

In the others the number of grains per square millimeter is shown in parentheses alongside the number.   Figure 79 shows the rela-

tion between average grain size and the hardness number in heat-treated steel, as obtained by Wood.

Figure 80 shows the surface of the metal in a polycrystalline specimen of iron before and after deformation. There is an increasing number of nearly parallel, fine lines across the face of each crystallite as deformation progresses.
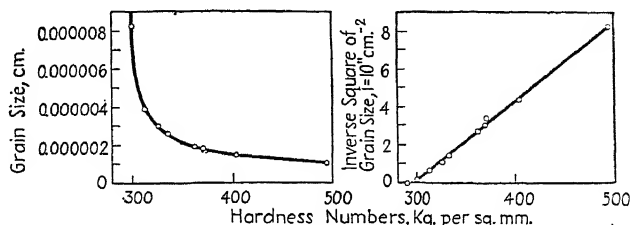
FIG. 79.—Relationship between grain size and hardness. (*After Wood.*) (*Courtesy of H. J. Gough and American Society for Testing Materials.*)

This experiment may be performed easily by gripping lightly in a vise a cube of copper or iron, the upper face of which is highly polished and etched to show the grain boundaries as in Fig. 80a. If a microscope is mounted over the specimen and the pressure on the specimen is increased gradually, fine dark

(a)   (b)

FIG. 80.—Structure of iron (a) before straining; (b) same field after straining. × 150. (*Rosenhain.*)

lines will appear in one grain, then in another, as is shown in Fig. 80b. These slip lines are, of course, the intersections of the slip planes (such as were found in the single crystals of zinc), with the plane of polish of the specimen. Slip occurs first in that grain whose orientation was such, with respect to the direction of the applied stress, that one of its planes of easiest slip was at 45 deg. to the direction of flow of the metal under the action of the force. A section through two of these grains at right

angles to the page would show the actual vertical displacement of the blocks with respect to each other. The slip lines appear black under vertical illumination because they reflect the light outside the microscope tube, as shown in Fig. 81. In oblique illumination they appear light. These lines disappear, of course, when the deformed surface is repolished.
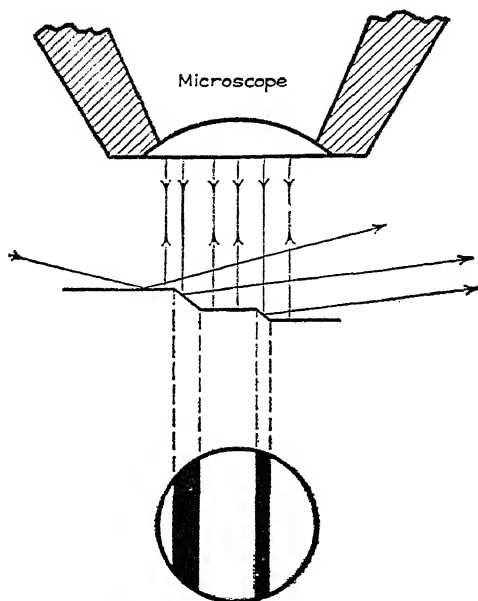
FIG. 81.—Diagram illustrating the optical behavior of slip bands.   (*Rosenhain.*)

In some metals the grains move with respect to each other before slipping begins within the grains. Tammann says this is the case for Fe, Ni, Zn, and Mg. In gold and copper the slip planes appear first.

As the plastic deformation of a polycrystalline metal proceeds, the individual grains elongate in the direction of flow. The progressive change of grain shape during the drawing down of a wire from 5 gage to 11 gage is shown in Fig. 82. The grains in a wire would be expected to become somewhat cylindrical or spindle shaped, whereas in rolling they would become thin, flat strips. Frequently plastic deformation and extensive grain distortion take place when it is not noticed, as in the shearing of sheet metal with a dull tool, as shown in Fig. 83. Slip in many grains and

in several directions in each grain accounts for the smooth and uniform spherical contraction at the "neck" of a polycrystalline iron tension specimen (Fig. 84), as contrasted with the flat fracture in a zinc crystal. Deformation of a polycrystalline body appears, therefore, more complicated than that of a zinc

CHEMICAL ANALYSES

Sample	C	M	P	S	Si
From 5 rod.....................	0.13	0.39	0.01S	0.037	0.106
Ladle test......................	0.11	0.39	.0.017	0.037	0.100
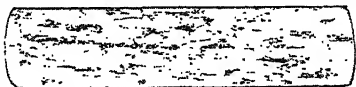
Gage	Diameter	Area	Number holes	Longitudinal microstructure 120 diameters	Tensile strength psi.	Elongation per cent in 2 in.	Reduction of area per cent	Per cent drawn reduction
5	0.215	0.03631	..		58,390	37.5	68.8	
7	0.180	0.02545	1		82,910	6.3	59.2	29.9
9	0.147	0.01697	2		96,900	4.0	45.0	33.3
11	0.120	0.01131	3		106,100	4.0	49.2	33.3

FIG. 82.—Grain elongation and change in properties of cold-drawn steel wire.

single crystal but quite comprehensible in terms of the single crystal.

Fiber Structure.—Just as deformation of the zinc single crystal in Fig. 60 is accompanied by a rotation of the slip systems into the tension axis, so in the deformation of a polycrystalline object, whether of zinc or any other metal, the principal planes of slip tend progressively to orient themselves parallel to the direction of flow of the metal as deformation proceeds. The structure so produced is called a *fiber structure*. It is illustrated schematically in Fig. 85b as contrasted with 85b. Fiber structure does not

become apparent until at least 30 to 40 per cent deformation has taken place.

Table V gives the fiber structures of a number of metals after deformations of two types—tension and compression. Fiber or

TABLE V.—DEFORMATION FIBER STRUCTURES (*Glocker*)

Mode of deformation	Lattice type	Metal	Directions parallel to direction of flow		Frequency of both positions
			Position I	Position II	
Tension	Cubic face-centered	Ag	[111]	[100]	II predominant
		Al	[111]	[100]	I strongly predominant
		Au	[111]	[100]	I and II equal
		Cu	[111]	[100]	I predominant
		Pd	[111]		
	Cubic body-centered	α-Fe	[110]		
		Mo	[110]		
		W	[110]		
	Hexagonal	Zn	[0001] 70° to tension		I preferred
Compression	Cubic face-centered	Cu	[011]		
		Al	[011]		
	Cubic body-centered	Fe	[111]		
	Hexagonal	Mg	[0001]		

texture structures in deformed metals are important in engineering work because the orderly alignment of the grains with respect to each other so produced results in marked directional properties in the object. It may be very weak if stressed in certain directions, and generally low in plasticity, as if it were coarsely crystalline. For example, extruded magnesium rods have the basal plane of the hexagon oriented parallel to the length of the rod. These rods are relatively weak in compression, having a yield point of 14 kg. per square millimeter as against 20 kg. per square millimeter in tension. Again, as the forging of magnesium alloys proceeds, further reduction becomes difficult because all the basal planes soon lie nearly parallel to the anvil. If a 30 per cent reduction by forging is followed by a 10 per cent stretch, partially *undoing* the previous step, a superior product is obtained at less cost.

Contrary to the original supposition, metals of the same lattice type do not always develop the same fiber structure.

Von Göler and Sachs[1] have shown that aluminum and silver, both face-centered cubic metals, do not develop the same fiber structure during rolling.

Rationalization of Certain Fiber Structures.—In the careful experiments of Taylor and Elam in stretching single crystal wires of face-centered cubic

Area covered by microphotograph
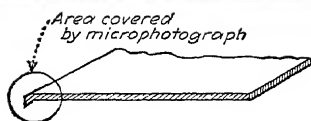
FIG. 83.

FIG. 84.

FIG. 83.—Burr on sheared edge of automobile sheet steel, showing grain deformation. (*Courtesy of Mr. Joseph Winlock.*)

FIG. 84.—"Neck," showing uniform contraction of a polycrystalline tension specimen. (*Sachs.*)

metals, such as aluminum, slip is found on the system (plane and direction) of highest resolved shear stress, with rotation so that the axis of the specimen and the slip direction approach each other, soon giving rise to a condition in which another slip system becomes equally stressed, whereupon both participate equally and the reorientation is now such as to bring a direction symmetrical to the two slip directions in question into the axis of the wire. This is the [112] direction which thus becomes the fiber axis in such single-crystal deformation. Passing on to polycrystalline deformation, the above

[1] *Z. Physik*, pp. 7–8, **56**, 1929.

fiber axis is not obtained because of restrictions or complications, in the slip process, of adjacent crystallites.   Actually, in stretching a polycrystalline face-centered cubic wire, [110] becomes the principal fiber axis, and E. Schmid has shown that this would indeed result from a process in which the three most highly stressed slip systems are considered to operate simultaneously.   Furthermore, the same method of analysis yields the second preferred fiber axis [100] in the case of grains originally found within a certain range of orientation.
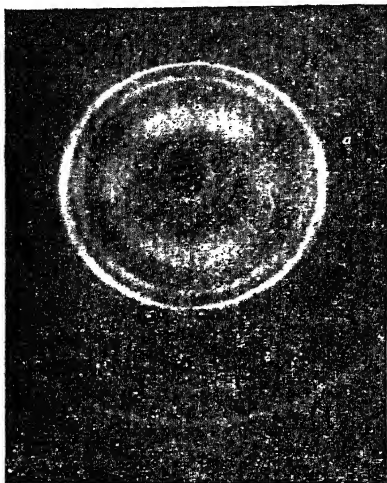
Fig. 85a.—Powder pattern of rolled steel sheet with randomly oriented grains, as indicated at *b*.   (*G. L. Clark.*)
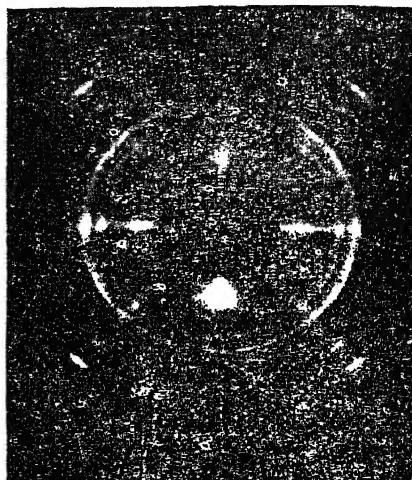
Fig. 86a.—Powder pattern of rolled steel sheet with marked fiber structure, as indicated at *b*.   (*G. L. Clark.*)
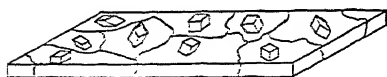
Fig. 85b.—Structure of sheet metal with randomly oriented grains.
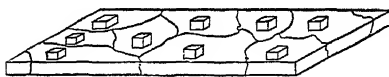
Fig. 86b.—Structure of rolled sheet metal (steel) with preferred orientation of grains.

Wever also obtains the principal fiber axis from an analysis based upon slip on the most highly stressed system together with rotation around an axis located in the slip plane at right angles to the slip direction.   (After partial deformation, a second system participates, as in the Taylor and Elam experiments.)

At elevated temperatures the slip system sometimes changes, as in the case of aluminum.   Above a certain temperature, slip begins to take place on the {100} planes in the [100] direction.   The entire hardening phenomenon changes.

Recent work of C. S. Barrett on the structure of α iron, after all ordinary types of deformation (drawing, rolling, compression, tension, and swaging), shows that the final orientation in all cases is a double texture with the [111]

and/or the [100] direction parallel to the axis of stress. Such a result may be predicted from Boas and Schmid's theory of deformation, but until Barrett's work, the mechanism of arriving at that orientation was not understood. Barrett showed that the mechanism actually involves a partitioning of the individual crystals into bands and the rotation of the material in each band toward the (100) or (111) positions, along the most direct route. The amount by which the orientation of each band varies from the original orientation of the crystal is small at first and increases with the amount of deformation. These bands will serve to explain many of the apparent departures of deformation from crystallographic laws when the deformation is severe. Barrett has observed deformation bands in single crystals and both coarse- and fine-grained polycrystalline aggregates.

Pole Figures.—The method of stereographic projection described on page 47 is frequently used to represent the orientations of the grains in a fibered object. Because the poles in a stereographic projection are true points, this method of representing orientations, strictly, can be used only for single crystals. However, its basic principles can be used to illustrate the positions of the individual grains in a polycrystalline aggregate. Such a diagram is called a *face pole figure*. This is best considered as a composite projection of the orientations of each of the large number of individual grains that constitute the aggregate. For simplicity, a separate pole figure is usually plotted for each of the two or three least complex families of lattice planes. It can be easily visualized that, if a completely random grain orientation exists, the individual poles would fall in every conceivable position on the projection and, as a result, the density of coverage would be uniform. On the other hand, if certain orientations are preferred by large numbers of grains, certain areas of the pole figure will become more densely populated. As this preference increases, the *extent* of these dense areas will decrease until the ideal position is attained for which all of the crystals have the same orientation, and the pole figure becomes a true stereographic projection (Dr. Carl Samans).

In Fig. 87, *a* and *b*, are shown face pole figures of the cube and octahedral planes, respectively, of a cold-rolled aluminum strip. In this representation the rolled strip is considered to be so placed that the rolling direction *D* is normal to the plane of the page and the surface of the strip is parallel to the top of the page, thus making the direction *P* normal to the rolling plane, vertical, and the transverse direction *C* horizontal. The shaded

areas, then, indicate stereographically the preferred positions of the poles in question.

If an octahedral, [111], direction is considered to be parallel to the rolling direction, *i.e.*, an octahedral pole at the point D, then cube poles can be located in the positions indicated by open circles in Fig. 87a, and octahedral poles in the corresponding positions in Fig. 87b. It can readily be seen that such a preferred orientation will, with a reasonable scattering, account for the shaded areas in both the pole figures.
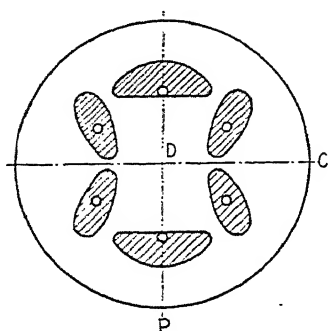
FIG. 87a.—Pole figure. Positions of cube faces in rolled aluminum sheet. (*Wever.*)
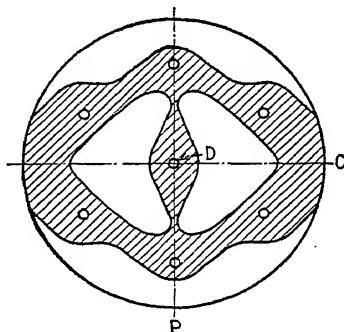
FIG. 87b.—Positions of octahedral planes in rolled aluminum sheet. (*Wever.*)

Flow Figures.—It can be proved mathematically that the maximum shearing stress in a specimen under tension or compression is at 45 degrees to the applied stress. Consequently, in a polycrystalline piece with slip planes available at all possible angles, slip will first take place at 45 degrees to the applied stress, and if the deformation is not homogeneous, the piece will deform locally along the plane of maximum shearing stress. This is the case in iron and most of its alloys. The local deformation is evidenced by lines on the surface which in tension are grooves and in compression are ridges. These flow lines are known as Luders' lines. In sheet-metal stamping and in deep drawing of sheets, they are called *stretcher strains.* Figure 88 shows flow lines in cast steel in the early stages of compression. Owing to a drop in yield point (described on page 325, Chap. XI, Testing), the flow at this region of maximum shear is extensive. Finally the region self hardens, perhaps by strain aging (*q.v.*), and flow begins in another region and is again self-stopping after a band

has formed.   The result is a network of depressed bands across the specimen, which sheet metal workers call *worms*.   When deformation is extensive, they spread and cover the entire surface and are no longer visible separately.

The Changes in Properties Accompanying Plastic Deformation.—That the properties of a metal should change appreciably when it is plastically deformed is perhaps surprising at first thought.   That these changes, particularly those in the mechanical properties of the metal, should be such as to *raise* appreciably

FIG. 88.—Flow figures in cast steel in the early stages of compression.   (*Meyer and Nehl*.)

the strength and hardness of the metal is even more surprising. It will therefore be quite interesting to examine these changes more closely and to see to what extent plastic deformation modifies each of the original properties of a metallic body.

Perhaps the most outstanding changes in a metal resulting from cold deformation are the changes in mechanical properties—the rise in tensile strength, yield strength, and hardness (not however the scratch hardness), and the decrease in plasticity and formability.   These changes are shown for a mild steel in Fig. 89 and nicely illustrated for cold-drawn wire in Fig. 82.   The yield strength of iron may rise from 25,000 up to 125,000 lb. per square inch.   The proportional limit of the metal rises also.   The modulus of elasticity may rise as much as 20 per cent in some s, but in steel it remains practically unchanged.

As is well known, a copper wire bent between the fingers becomes harder at the bend. As the hardness rises the formability falls, causing the wire to break off short after several bends. The copper wires for electric power transmission are hardened and strengthened by being drawn through the die. Their elastic limit is raised. Hence longer spans between poles can be used without danger of the wires breaking in a storm. The metal
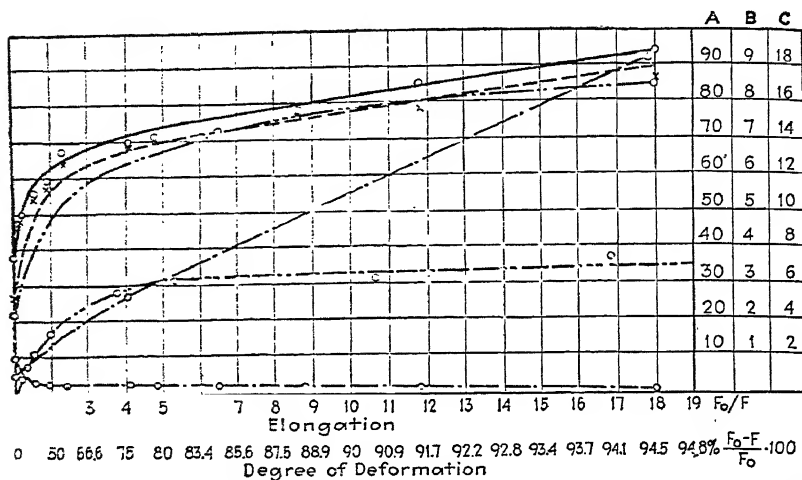
FIG. 89.—The change of mechanical properties of mild steel by cold working.
(*Altpeter in Sauerwald.*)

(A) ——————— Tensile strength, kilogram per   — · · — · · — Scleroscope hardness A
square millimeter
(A) — — — — Yield point, kilogram per square   — — · · — — · · Solubility rate B
millimeter
(A) — — · — —. Elongation, per cent   — · — · — · Elongation of crystallites C

immediately adjacent to a punched rivet hole is hardened in this way also. The new streamlined trains are made of stainless steel, whose elastic limit has been raised from some 80,000 up to 150,000 lb. per square inch by cold rolling.

This ability of metals to harden under deformation is of very great importance in another way. Pitch or molasses if pressed into a die would yield at one point, become thin and tear through at this point. In metals the thin part hardens and shifts the deformation to the thicker parts, thus causing a uniform deformation instead of a localized one. Without this property of *work hardening* all deep drawing of metals would be impossible.[1]   Not

[1] Imagine, for instance, trying to form a felt hat by deep-drawing a flat sheet of felt.

all of the properties, however, are improved by deformation. If a severely deformed material is placed in service, it will be unable to sustain plastic deformation due to overload, but will be brittle and likely to break under such stresses. The impact resistance diminishes so that, for example, a heavy crane chain when overloaded will stretch plastically and thereafter be weaker against sudden impact.[1]

As was stated in Chap. I on page 28, Smekal has divided the properties of metal into two groups, the structure sensitive and structure insensitive properties. The structure insensitive properties are little affected by cold forming, and their changes are in general relatively unimportant. For example, the specific volume decreases only slightly (increase in density) during the early stages of deformation, probably as a result of the closing up of voids and pores, and with further deformation, increases a fraction of a per cent. The decrease in density may be sought in the formation of minute cracks or "space canals" within the object, produced by extensive deformation.

In the structure sensitive properties, however, the changes are sometimes of great importance. The specific electrical resistance increases sometimes by several per cent. In the case of tungsten, Geiss and van Liempt report an increase of 50 per cent in the resistance when the tungsten is reduced 99 per cent in drawing.[2] The temperature coefficient of resistance also changes in accordance with the Mattheissen law that the product of the specific electrical resistance and the temperature coefficient of resistance is equal to a constant.

The magnetic properties of the ferromagnetic metals are greatly affected by deformation. The saturation magnetization, the susceptibility, the permeability, and the remanent magnetism are, in general, lowered, while the coercive force is raised, and the hysteresis losses are increased. The very high permeability of "Permalloy" is largely destroyed by very slight deformation.

The changes in electrochemical potential and free energy upon cold work are shown in Table VI (Sauerwald). The change in electropotential is important because the e.m.f. set up in sections of a nonuniformly deformed piece, *e.g.*, a bent pipe or a punched rivet hole, may lead to rapid electrolytic corrosion at the

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[1] The theories of work hardening will be discussed later.

[2] GEISS and J. A. M. VAN LIEMPT, *Z. Physik*, **41**, 867, 1927.

deformed region in the presence of an electrolyte such as salt or alkaline water. The rate of solution and heat of solution of uniformly deformed metal increase with cold work; in fact, both qualities have been used as a measure of increase in internal energy.

TABLE VI.—CHANGE IN E.M.F. AND IN FREE ENERGY BY COLD WORKING
(*Sauerwald*)

	Change in e.m.f. ΔE	Valence	Change in free energy per gram-atom	
			Calories	Ergs
Sn	+0.00011	4	10	$4 \cdot 10^8$
Pb	+0.00012	4	6	$25 \cdot 10^8$
Cd	+0.00020	2	10	$4 \cdot 10^8$
Ag	+0.00098	1	25	10^9
Bi	+0.0002–0.0005	3	40	$15 \cdot 10^8$

The thermoelectric force changes during deformation, so that a thermocouple may be made of a cold-drawn wire and an annealed wire of the same material. This fact explains the necessity of using unstrained wires in the resistance pyrometer.

The color changes, the rate of vaporization rises, as does also the rate of diffusion, as a result of cold deformation.

Thus, although there are important and interesting changes in many metallic properties upon deformation, yet it is clear that the most striking and extensive are the changes in mechanical properties, particularly those of strength and formability.

Internal Stress.—In addition to the changes in physical and chemical properties, internal stresses, often of a very high intensity, may be left in an object after cold deformation. In this condition, the object is susceptible to spontaneous cracking, called *season cracking*, especially if subjected to corrosive action such as sea water and industrial gases supply. These internal stresses represent an increase in internal energy. Hort finds an increase in internal energy of from 0.9 to 5 cal. per gram-atom of deformed material. Other investigators find that the total internal energy of the object increases 13½ per cent for steel, 8 to 9½ per cent for copper, 7 to 8 per cent for aluminum, with drastic deformation.

The presence of internal stresses may be revealed[1] by taking a light cut off the surface of a cylindrical bar that has been cold drawn. The *length* of the bar increases after each cut; or layers may be removed by dissolving them in acid. Plotting the stress distribution (calculated from the change in length and the modulus of elasticity of the metal) throughout the cross section of a cold-drawn bar of nickel shows, in Fig. 90, that the surface layers of such a bar are in tension, while the core is in compression. Removal of the surface layers (in tension) permits the compressed
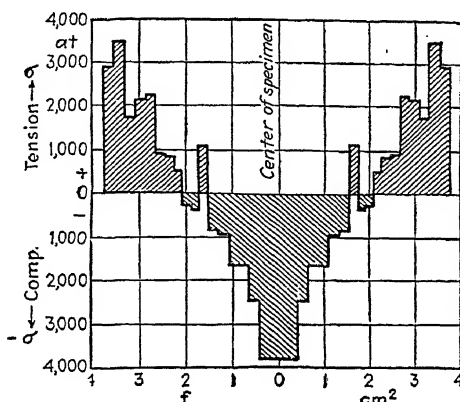
FIG. 90.—Distribution of internal stresses in a bar of cold-rolled nickel. (*Heyn.*)

core material to expand and the piece to lengthen. In rolling, this stress distribution is caused by the lesser extension of the surface layers of the object, which are gripped by the rolls, as compared with the greater extension of the core. These internal or initial stresses may be as high as 20,000 or 30,000 lb. per square inch or higher. If a nonplastic member of a structure were understood to have a tensile strength of 40,000 lb. per square inch and contained an internal stress of 30,000 lb., when only 10,000 lb. external load had been added, it would fracture.

Attempts to Explain Work Hardening.—We have now noted the more important changes in properties that accompany polycrystalline deformation. We have surveyed previously the mechanism of deformation in a single crystal and in a polycrystalline body. It remains now to attempt a logical explana-

[1] The internal stresses in cold-drawn brass tubing are nicely revealed by immersing it in a solution containing 100 g. $HgNO_3$, 13 cc. HNO_3 in 1,000 cc H_2O. The tubing splits almost immediately.

tion for these changes in properties on the basis of what we know of metallic structure, and of the observed changes in this structure during deformation. Since the change in hardness is of very great importance, it has received the most attention.

With X rays as tool for investigating structural changes during deformation, the following observations have been made. (1) Soon after deformation begins, the lattice shatters into small crystalline fragments of a size estimated to be of the order of 10,000 times the interatomic distance. The shattering is revealed by the sudden transition of the transmission photograph from the widely separated spots of a coarse-grained specimen to the sharp continuous rings of a specimen of grain size between 10^{-3} and 10^{-6} cm. Crystal breakup in excess of that established by the first lattice shattering evidently does not take place, since no diffusion of the continuous rings appears as deformation proceeds. (2) As slip proceeds, a preferred orientation develops, *i.e.*, the planes of slip rotate into the plane of the applied force. As the plane of slip approaches parallelism with the line of the applied force, the component of that force parallel to the slip plane diminishes and a higher applied force is necessary for the continuation of the slip process. (3) A Debye pattern shows that the crystallographic dimensions of the metal are essentially unchanged, regardless of the amount of deformation. Any distortion of the lattice itself that takes place is within the elastic range and rapidly approaches a maximum.

Slip Interference.—It would seem that the shattering of the lattice, mentioned above, would afford an excellent means of explaining work hardening, in that the crystalline fragments formed would have their slip planes in disregistry with those of neighboring fragments and thus obstruct further slip. However, it has been shown that it is possible to remove the effects of work hardening by heating the metal without removing the fragmented structure.

Orientation Hardening.—The development of a preferred orientation as exemplified by the fiber structure formed in wire drawing must certainly contribute to work hardening. However, such a preferred orientation does not develop until the metal is 30 to 50 per cent deformed, and since work hardening begins as soon as deformation begins, change in orientation cannot be considered a fundamental cause of work hardening.

Elastic Distortion.—Lattice distortion in the elastic range indicates the bending of slip planes and an increase of internal energy. Such bending and roughening of atomic dimensions can conceivably increase the frictional resistance to slip. However, lattice distortion rapidly approaches a maximum value, and for some metals which display marked work-hardening tendencies, *e.g.*, Al, Pt, and Mo, lattice distortion is negligible.

More Recent Theories.—W. G. Burgers has introduced a theory in which he proposes that slip is of a localized nature and that such localized slip regions are accompanied by a curvature at their ends that hinders further slip. The total work hardening
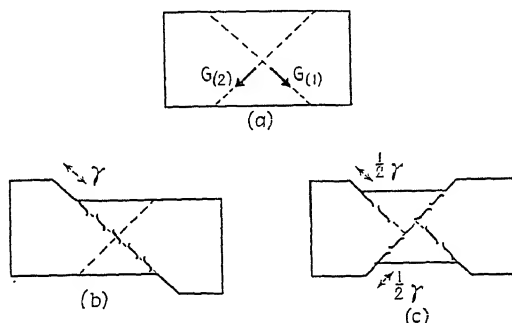
Fig. 91.—Schematic representation of local curvature along glide planes: for a given total shear γ the average degree of bending is greater in case of gliding along on (*b*) than along two (*c*) glide planes. (*Courtesy of W. G. Burgers.*)

is then a function of the total number of curved regions, and the degree of curvature of each. Figure 91 shows schematically the representation of local curvature.

M. J. Buerger has advanced an interesting theory of work hardening in connection with his lineage theory of metals. The lineage theory proposes that when metal crystals grow from their nuclei, temperature gradients, foreign atoms, and the mechanism of growth combine in such a way as to force sections of the crystal out of any geometrically perfect orientations with respect to each other. The result of this crystal imperfection would be that ever-increasing slip would cause an ever-increasing disregistry of the atoms of one slip plane with respect to the atoms of the adjacent slip plane beneath it, as illustrated diagrammatically in Fig. 92. Sections *a* and *b* are two portions of the same crystal separated by a lineage boundary, and the plane of the paper represents the slip plane. If the plane just above

the one represented, slips in the direction of the arrow, the dis-
registry is apparent. The increased energy content of the
deformed metal may be due to the final nonequilibrium position
of the atoms in one plane with respect to another.

The most recent theories, mainly those of Polanyi, Orowan, and
Taylor, are based primarily on the assumption that the strength
of the crystal is fundamentally that which may be calculated
from physical constants of the lattice, and not that which is
observed in experimental measurements.
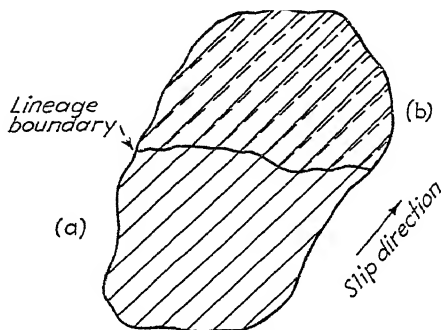
FIG. 92.—Schematic illustration of the disregistry of slip planes in a crystal having
a lineage structure.

These experimentally observed strengths are supposed to arise
from the planes of weakness in the crystal. When stress is
applied, the weakest of these planes slips first and as this plane
work-hardens, the deformation shifts to progressively stronger
planes, requiring, therefore, progressively higher stress.

This type of approach eliminates the necessity of explaining
work hardening on nonoperative planes. The degree of perfec-
tion of the slip planes, and their orientation with respect to the
applied stress, determine upon which of the planes localized
slip occurs. As slip proceeds, mutual interference of localized
slip areas and elastic distortion serve to stop slip, and some other
plane in the crystal, which was less weak originally, slips. The
weakness of each plane is determined by its degree of perfection.
The limiting strength for any plane is the theoretical strength
of the lattice. This type of explanation is new, but it presents
great possibilities.

We are left, therefore, without any entirely satisfactory
explanation for the important changes in properties which we
have observed to result from the deformation of metals.

The mechanism of deformation, however, seems now clearly described: Slip takes place accompanied by rotation of the crystal. It begins in that grain which has its plane and direction of easy slip most favorably oriented with respect to the applied force. Slip resistance increases in this plane, and other planes parallel to it begin to slip. Eventually other planes in the same grain, and planes in other grains, begin to slip. Twinning may occur, and when it does it usually presents a more favorable orientation for slip. Finally most of the grains have taken up a symmetrical orientation with respect to the direction of stress; cracks and internal fissures open up, and the specimen parts.

The Amorphous-cement Theory.—No discussion in the English language of the causes of work hardening would be complete without mention of the amorphous-cement theory proposed originally by Beilby and modified notably by Rosenhain and by Jeffries. This theory postulates that films of atoms in the disordered or amorphous state are left between each of the grains of a casting after solidification is complete. These atoms are attracted equally by the two neighboring lattices and therefore join neither of them. Since these atoms are not in any crystal, they constitute "amorphous" metal. This "amorphous metal" is similar in properties to liquid metal, in that it is lower in conductivity and density, etc., than crystalline metal; but as a supercooled liquid, like glass, is hard at room temperature, being high in viscosity and having no slip planes, so this amorphous metal is assumed to be hard at room temperature, and to increase the hardness of the entire piece of metal in which it exists as a continuous network.

Deformation of a metallic object at temperatures far removed from the melting point is understood to increase the quantity of amorphous material in it. This increase takes place in two ways: (1) The movement at grain boundaries during deformation increases the thickness of the existing intergranular films by tearing atoms out of the contact surfaces of adjacent grains, and (2) slip *within* the grain results in tearing atoms out of the opposite faces of the slipping planes and thus produces films of amorphous metal within the grains. The increase in hardness of the metal is understood to be due to the increase in amount of this hard, amorphous material at the grain boundaries and in the slip planes.

The decrease in density accompanying cold work is understood likewise to be due to increase in the amount of amorphous material. The decrease in electrical conductivity of the object is finely explained on the same basis, as is also the increase in e.m.f., and rate of solution, since liquid metal partakes of these changes in properties, *i.e.*, decreased density, conductivity, and resistance to solution, as compared with crystalline metal.

While glass is very hard at ordinary temperatures, it softens at higher temperatures and flows easily. Metals stressed slowly at elevated temperatures fail, not by transcrystalline fracture as they do at lower temperatures, but by intercrystalline fracture, shown for a bronze specimen in Fig. 29. This pulling apart of the grains at higher temperature is said to be due to the rapid softening of the amorphous material (decrease in viscosity) as compared with the slower softening of the crystalline grains as the temperature is raised. Obviously, at some temperature the cohesion at grain boundaries will be just equal to the crystalline cohesion. This temperature is called the *equicohesive temperature* and has been determined for several metals. The amorphous-cement theory thus explains well many of the experimentally observed properties of metals.

It meets, however, with almost insurmountable objections. The postulated presence of considerable quantities of amorphous metal at temperatures so far below the melting point is difficult to accept even as a surface phase. Again, it is observed that whereas a metal hardens during tension, reversal of the applied stress, *i.e.*, compression following stretching, actually shows less hardening or even softening as compared with the original state. To account for this fact, it would be necessary to assume anisotropism and therefore directional properties in the amorphous (isotropic) cement. Furthermore, investigation of a polished metal surface by X rays at a glancing angle reveals that it is crystalline, not amorphous as Beilby originally supposed. These and other objections have led to the discarding of this useful theory by most authorities in the field. The theory is valuable, however, as a means of remembering the nature of the changes produced in metals by deformation.

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THE ANNEALING OF DEFORMED METAL

Purposes of Annealing.—The question of work hardening and the accompanying change in physical properties may at first seem to be of only academic and theoretical interest, but a glance at Chap. IX, The Shaping of Metals, will impress one immediately with its widespread industrial importance. In drawing metal wire through a die, in the manufacture of wire, the metal work-hardens, and the resistance to further deformation increases. The power required to continue drawing increases, and finally the resistance to deformation equals the resistance to fracture and the wire will break upon further stress application. If the wire is used in the hardened condition, its conductivity is lowered, it is brittle toward impact loading, its magnetic permeability is decreased, and its corrosion resistance is lowered. Such a wire would be highly undesirable in most industrial applications. Similar changes in properties are encountered in deep drawing of metal sheet, in stamping, and in forging. It is conceivable that the increase in strength and decrease in other properties might be desirable, but if further deformation is necessary in order to obtain the required shape, or if it is necessary to utilize the maximum electrical conductivity and magnetic permeability, it is imperative that the metal be somehow returned to its original

condition as regards physical properties. The process through which this result is achieved is known as *annealing*.

Instability of the Deformed State.—Whatever theoretical explanation of the work hardening of metal is adopted, the work-hardened state, with its high hardness and strength, decreased plasticity, lowered conductivity, lowered magnetic permeability, and increased energy content, must be regarded as one of unstable equilibrium. If the temperature is raised, equilibrium begins to return, and the normal properties of the metal are gradually recovered. The shape as given the object by cold working, however, remains unchanged. The heating of a cold-worked metal to or above the temperature at which equilibrium begins to return is called *annealing*.

General Relationships.—The effect of heating on cold-worked metal may be divided into two general stages: (1) recovery and (2) recrystallization.

The two stages are shown schematically in Fig. 93. The period of recovery is an interval during which the original properties tend to be recovered without any accompanying change in microstructure. It is essentially a low-temperature phenomenon, and is probably due to a great extent to the removal of most of the internal stress. The recrystallization period, which proceeds at a higher temperature than recovery, is an interval in which entirely new, strain-free crystals are formed from the deformed metal. The physical properties are all recovered in this period. Grain growth proceeds with increasing temperature or longer time following the formation of these strain-free crystals by the coalescence of some of the new grains formed. The properties change, commensurate with an increase in grain size. The change in tensile properties of Cu on cold rolling and annealing is shown in Fig. 94.
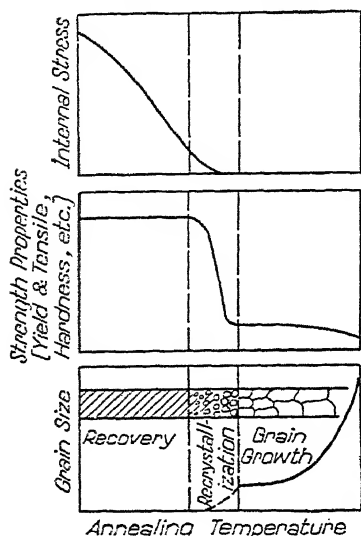
Fig. 93.—Schematic illustration of the variation of internal stress, strength properties, and grain size of work-hardened metal with temperature. (*After Sachs.*)

It is impossible to state a definite temperature at which each one of these stages takes place, for the changes are affected by so many variables.   Increasing the time of annealing tends to lower the initial temperature for each stage to begin.   Increasing the amount of deformation prior to annealing has the same effect because the increased instability of the more highly deformed state requires less energy to initiate the change.   Decreasing the purity of the metal displaces each of these periods to higher temperatures.   Increasing the temperature of annealing decreases the
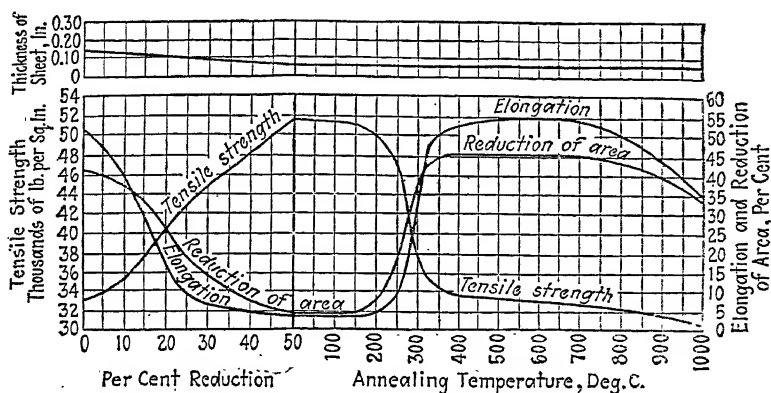
Fig. 94.—Effect of cold rolling and annealing on the properties of copper. (*Mathewson and Thalheimer.*)

time interval necessary for each effect to be completed, and the higher the temperature, the more difficult it is to distinguish the periods.   In low-melting metals it is difficult to distinguish the stages because, even at room temperature, the metal is very near its melting point, and the resistance of the lattice to structural changes is low, so that the various stages in annealing take place rapidly.

Recovery.—As the temperature of a cold-worked object is gradually raised, the first change that takes place is the relief of internal stress.   The displaced atoms in the elastically distorted lattice spring back to their original positions, the elastic properties are recovered, and conductivity and magnetic permeability increase without any visible accompanying change in microstructure.   A "light anneal" will relieve these stresses, but not quite completely and without appreciable loss of hardness and strength of the metal.   In fact, the hardness may rise slightly. For instance, cold-worked brass, such as cartridge shells and

condenser tubing, annealed at 200° to 250°C., are freed practically (although not entirely) from internal stress and enjoy a slight increase in tensile strength over the cold-worked condition. This increase is more than likely, owing to a process known as *strain aging*, similar to age hardening, which will be discussed in a later chapter. The low temperature required for stress relief makes the process slow and often costly.

Recrystallization.—In the deformation of a metal, we have seen that slip takes place along definite crystallographic planes in definite directions and that slip results in a distortion of the slip planes and grain boundaries, with an accompanying increase in internal energy. We should expect that energy increase to be located on the slip planes and in the grain boundaries, as there are the points at which the actual deformation takes place. Thus at definite points throughout the deformed metal there are localized regions of high-energy content. The amount of deformation determines the number and magnitude of these high-energy areas. Now if the temperature of the metal is raised, the energy content of the entire piece is raised. When the temperature is reached at which the localized areas have sufficient energy to overcome the rigidity of the distorted lattice, they give up their energy as a heat of recrystallization, and form nuclei for the growth of new, stress-free crystals from the surrounding distorted metal. The number of nuclei precipitated depends upon the amount of previous deformation, the number increasing with increasing deformation. The number of nuclei also depends upon the temperature of anneal; the higher the temperature, the more areas will be raised to an energy level sufficiently high to precipitate nuclei. The first point to precipitate a nucleus will be the area in which the concentration of energy, due to cold work, was the highest. With the proper choice of degree of deformation and annealing temperature, it is possible to form only one nucleus, *i.e.*, to grow a single crystal from a large volume of polycrystalline material.

Figure 95 shows recrystallization schematically.

Just as nuclei form and grow in the freezing of a liquid metal, gradually consuming this liquid, so nuclei form and grow in cold-worked metal when the temperature is raised, gradually consuming the cold-worked material. Here the analogy breaks down, for cast grains, being surrounded by more or less continuous

films of insoluble impurities, are largely prevented from coalescence across these barriers, while in cold-worked metals these films are broken down by the severe working and can offer no resistance to further growth by coalescence.

Fundamental physical theory tells us that small particles have a higher free-energy content than large particles have. This fact, coupled with the consideration that at each temperature a body tends to approach its lowest energy level, means that grains will coalesce, so that *under ideal conditions* the metal would exist
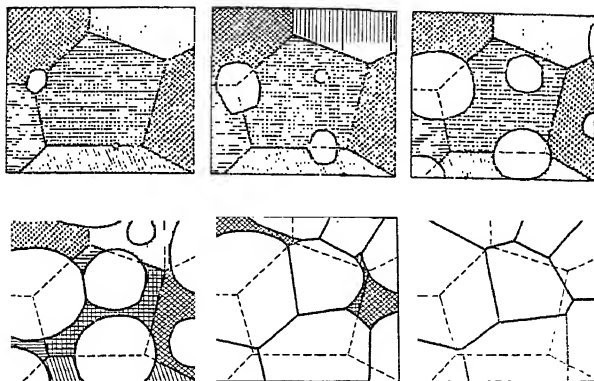
FIG. 95.—Schematic illustration of crystal growth in a recrystallizing metal. (*R. F. Mehl.*)

as a single crystal and in its lowest energy state. Opposing the tendency to form a single crystal is the rigidity of the lattice. Increasing the temperature decreases the rigidity of the lattice. At any given temperature there exists a maximum grain size at which the two opposing tendencies are at equilibrium. Time, of course, affects the balance; short times at temperature give less opportunity for the balance to be attained.

Upon the completion of the recrystallization period, the metal is composed of practically stress-free crystals and most of the original physical properties are recovered, their absolute values being established by the final grain size attained in the process of nucleation and grain growth.

By holding the time factor constant, the relationship of deformation, temperature, and the resultant grain size may be shown in a three-dimensional diagram, as illustrated for 0.18 C steel, in Fig. 96.

It can be seen that at low degrees of deformation the grain sizes are the largest, owing to the fact that the number of initial nuclei precipitated were few and the consequent number of grains were few. As the degree of deformation increases, the number of nuclei precipitated increases, and the temperature for initial recrystallization decreases. The larger grain size at higher temperatures is due to coalescence.

We can present the following fundamental laws dealing with recrystallization: (1) A certain minimum amount of cold work and
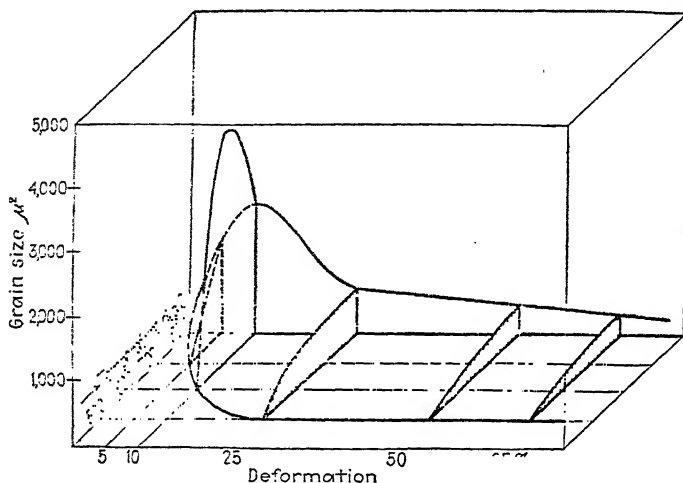
Fig. 96.—Recrystallization diagram of a 0.18 per cent carbon steel. No change is observable after one hour of anneal. (*Oberhoffer and Jungbluth.*)

a certain minimum temperature are necessary for recrystallization to occur. (2) The less the amount of cold work, the higher the temperature for initial recrystallization. (3) Longer annealing times decrease the temperature necessary for recrystallization. (4) The final grain size is dependent primarily upon the degree of deformation and to a lesser degree on the temperature and time of anneal.

Figure 97 shows nicely the change in microstructure upon the annealing of cold-drawn cartridge brass at a series of temperatures. At 350°C. recrystallization is complete, and at temperatures higher than that grain growth proceeds.

Figure 98 shows strikingly the effect of different amounts of cold work upon the grain size resulting from recrystallization of

(a) Cold worked.   (b) 300°C.

(c) 350°C.   (d) 450°C.

(e) 550°C.   (f) 650°C.

(g) 750°C.   (h) 800°C.
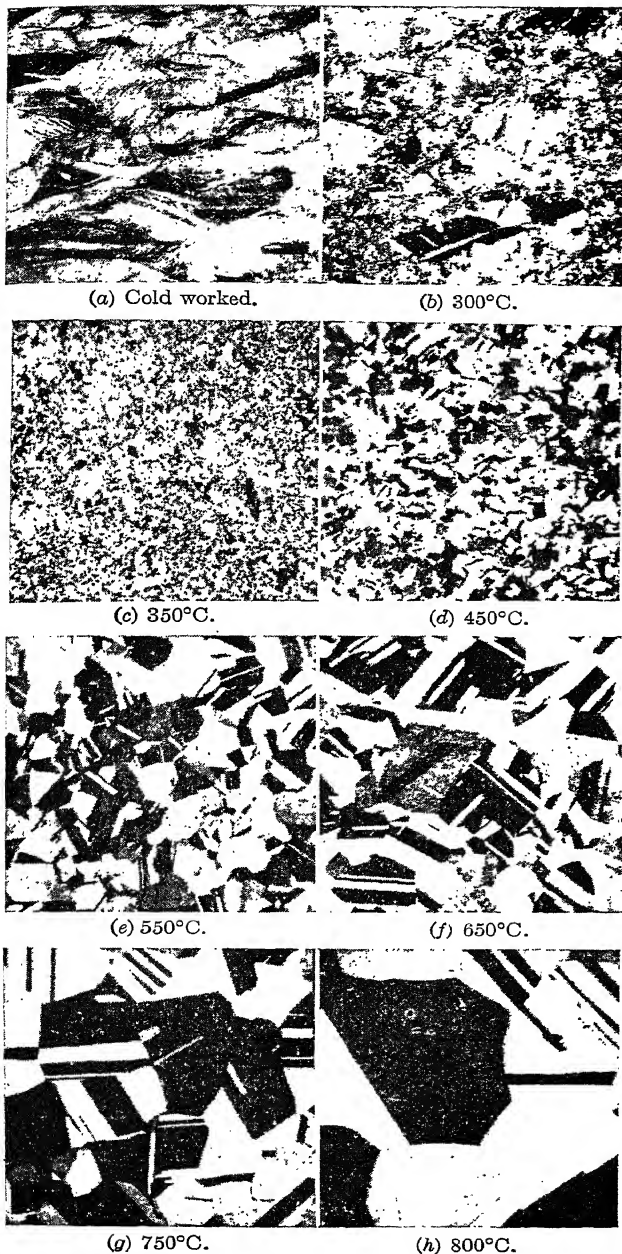
Fig. 97a–h.—Stages in the annealing of cold-drawn cartridge brass.   (*Courtesy of Mr. N. H. Muraza.*)

tin.   The picture is that of a recrystallized sheet of tin through which two bullets had previously been shot.   The deformation varies from a maximum at the holes to almost zero.   The recrystallized grain size increases from the bullet hole outward until a maximum is reached where the amount of deformation

Fig. 98.—Tin sheet showing bullet holes and grain size after annealing at 200°C. × 2.   (*Czochralski.*)

is the minimum necessary for recrystallization to occur.   Beyond that point the original grain size is encountered.

Since coarse-grained material is usually quite brittle, it is clear from the above illustration that, if some parts of an object are slightly deformed in manufacture, while other parts are highly deformed, there is danger that annealing will result in a very coarse grain size in the slightly deformed parts, with accompany-

ing brittleness. For example, when a low-carbon steel pipe is bent and then annealed at a high temperature (but below the temperature of polymorphic transformation in steel, $\alpha - \gamma$), a very coarse grain size develops in the regions of very slight deformation adjacent to the bend. These regions will be brittle. Since these slightly deformed parts will require a higher temperature than the more drastically deformed parts, in order to produce a change in grain structure, the difficulty may be avoided by using a lower annealing temperature and a longer time of anneal. This remedy, of course, sometimes interferes with low-cost production schedules.

Fiber Structure in Annealed Objects.—Instead of a random orientation, recrystallization may lead to a fiber structure. The fiber structure after annealing may be identical with the deformation fiber structure produced by cold deformation, or it may be a different one. The recrystallized fiber pattern for several metals is given in Table VII.

TABLE VII.—FIBER STRUCTURE OF RECRYSTALLIZED METALS INSOFAR AS THEY DIFFER FROM DEFORMATION FIBERS *(Sauerwald*

Mode of deforma-tion	Lattice type	Metal	Recrystal. temperature, °C.	Crystal orientation	Remarks
Drawing	Cubic face centered	Cu	>1000	[112] Axis of wire	Al very pure 99.7% Ag
		Al	>300	[100]	
Rolling		Ag	250–800	[112] WR (113) WE	
		Cu	250–1050	[100] WR (001) WE	
		Al	....	....	
		α Brass	300–700	[112] WR (113) WE	

WR = direction of rolling. WE = plane of rolling.

Summary.—The effect of heating cold-worked metal may be divided into two stages: (1) recovery—removal of internal stress and partial recovery of some of the physical properties without a change in microstructure; (2) recrystallization—formation of new, stress-free grains, absorption and coalescence of these grains formed, and recovery of most of the physical properties.

Four fundamental laws of recrystallization are (1) a certain minimum cold work and temperature are necessary for recrystallization; (2) the lower the degree of cold work, the higher the temperature necessary for recrystallization; (3) longer annealing

times decrease the temperature necessary for recrystallization; (4) the final grain size is dependent primarily upon the degree of cold work.

HOT WORKING

The Importance of Hot Working.—A great number of metal shapes used today are formed or fabricated from cast ingots. For example, a normal ingot size for steel to be used for mass production purposes is from 18 to 36 in. square in cross section and from 68 to 74 in. high. It is from such ingots that metal plate, sheet, wire, rails, beams, etc. are produced, because it has been found the most economical means of obtaining the required combination of shape and properties. The drastic reduction necessary to produce these thinner sections is most rapidly accomplished, and with a minimum of power and of wear on the machinery, when the metal is in a hot and plastic condition. Some of these hot-worked products constitute the raw materials used for subsequent cold-forming operations.

Aside from the economy angle, there are some metals, *e.g.*, W, Mo. and Zn. that cannot be deformed in the cold state without cracking, but must be deformed in the hot-working temperature range in order to remove or alter the "as cast" structure. The metal is thus conditioned for subsequent cold work. Other metals are so hard that they never lend themselves economically to deformation at low temperatures.

What Is Hot Working?—During hot working both of the phenomena previously examined—hardening due to deformation and softening due to annealing—occur simultaneously. If deformation is carried out more rapidly than softening can take place at that temperature, the metal will harden. Figure 99 shows that in the slow deformation of copper in a tension test the rate of softening increases with increase in temperature. The graph indicates that at about 400°C. the rate of softening will equal the rate of hardening, and the metal can be continuously deformed thereafter without increase in stress as deformation proceeds. If the deformation is rapid, as in hammer forging, the temperature at which the two rates are equal is higher (800°C.), as shown in Fig. 100. Metals never cease to work-harden up to a temperature very near their melting points, but the rate of work hardening constantly decreases with increasing temperature.

This may be explained to a great extent by the fact that at higher temperatures a larger number of slip systems are operative and that the lattice is less rigid. For a given rate of deformation there exists a definite temperature at which the hardening is just balanced by simultaneous softening. Above this temperature deformation is termed *hot working;* below it, *cold working.* Thus, from the standpoint of its effect on the properties and structure of the metal, the temperature at which working is done is not significant unless it is accompanied by some knowledge of the rate at which deformation proceeds. Steel forged at 500°F. is
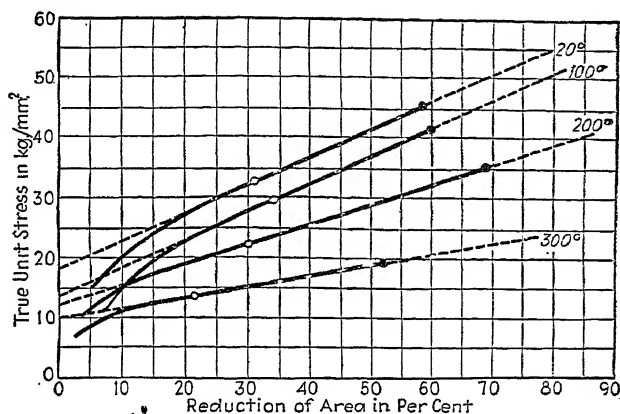
Fig. 99.—Hardening of copper in tension test at various temperatures. Rise in true unit stress indicates rise in hardness. (*Körber and Rohland.*)

said to be *finished cold* while lead worked at room temperature is being hot worked.

Finishing Temperature.—If the deformation is completed while the object is at a temperature far above the recrystallization temperature (*high finishing temperature*), then, during cooling down of the object to this temperature, grain growth progresses. This leads to a coarse grain size in the final object and to a low value of contraction of area in the tension test. If, on the contrary, deformation is continued until the temperature of the object is below the recrystallization temperature (*low finishing temperature*), the plasticity of the metal may be insufficient and the object may crack in the operation. In the tension test, metal finished too cold will show a high yield point but rather low contraction of area and elongation. The optimum finishing tem-

yielding the finest grain size is, therefore, that which is as possible to the recrystallization temperature but
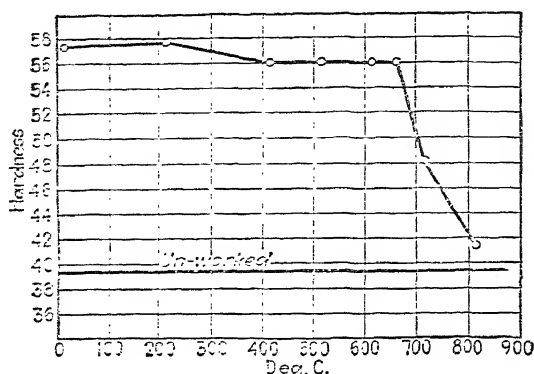
Fig. 100.—Hardness of copper after quenching from forging temperatures. *(Sauerwald and Giersberg.)*
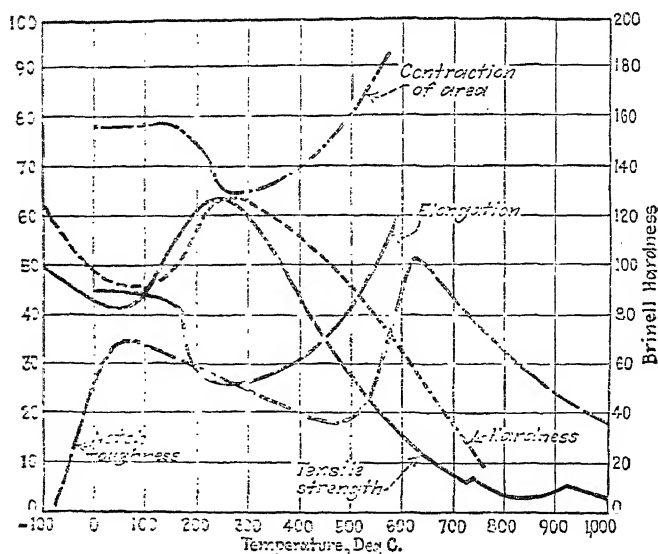
Fig. 101.—Dependence of tensile strength, elongation, notch toughness, and hardness of mild steel upon temperature.   *(Oberhoffer.)*

slightly above it. Since the center of the object is likely to be hotter than the exterior, it is the surface temperature that is used as a guide. The grain size at the center will therefore be coarser than that at the surface (see also Shaping in the Solid

State, page 289). Figure 100 shows the effect of *finishing temperature* on the hardness of quenched-copper forgings.

The Formability of Metals at Various Temperatures.—As was mentioned at the beginning of this section, in general, the formability of metals increases with rise in temperature and their resistance to deformation decreases (Fig. 101). Thus forging, rolling, and stamping are usually, but not always,
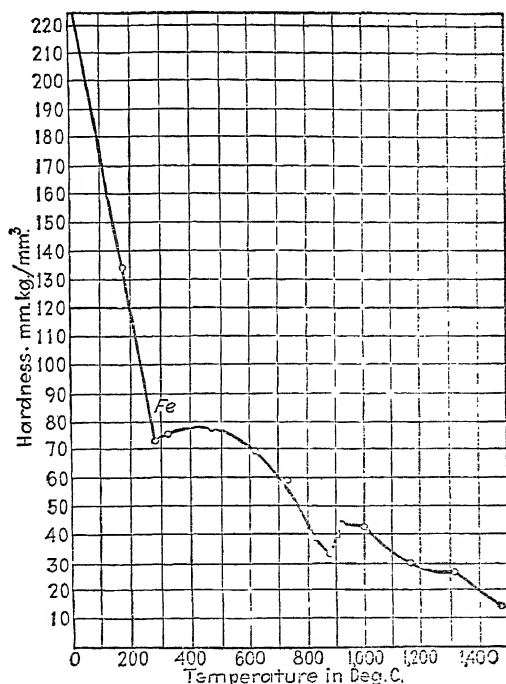
Fig. 102.--Hardness of electrolytic iron at various temperatu   (*Sauerwald and Knehans.*)

done upon hot objects, while extruding is usually done as near to the melting point as possible. The velocity of extrusion often doubles for a 10°C. rise in temperature. There is thus less energy required in hot working and less danger of fracture or cracks. If the metal exists in a new polymorphic form at the higher temperature, however, as γ iron above 910°C., the formability may decrease suddenly at a certain temperature, as it does in iron (Fig. 102). In metals and alloys, there are important exceptions to this rule as, for example, the brittleness of iron and

zinc below room temperature and of steel slightly above room temperature, the so-called *blue brittleness,* as illustrated in Figs. 101 and 103.
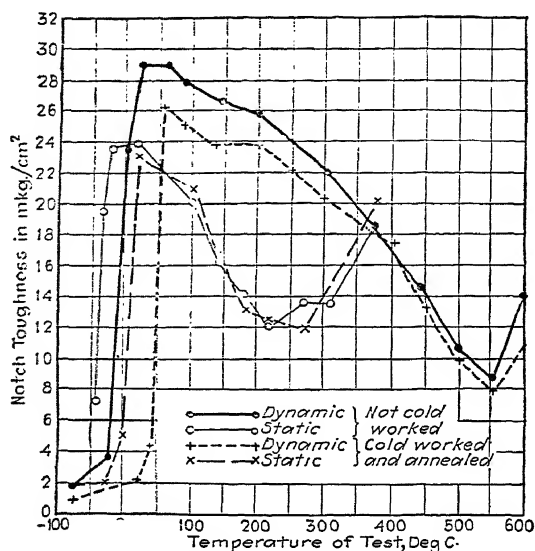
Fig. 103.—Static and dynamic notched bar tests at various temperatures with cold-worked and with annealed mild steel.   (*Mailänder.*)
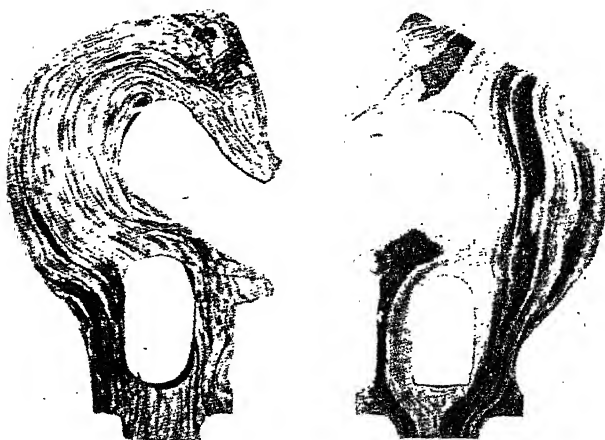
Fig. 104.—Two railway draw hooks, one formed by bending, the other cut from a straight piece.   Note the crack in the latter hook.   (*Frémont.*)

The Properties of Hot-formed Metals.—In addition to producing the desired thin sections most economically, hot working

improves the properties of the metal as cast. Not only are there a refinement of grain size and a partial elimination of preferred orientation or cast structure, but deformation and annealing also crack up the shells of impurities encasing the grains and permit by diffusion the elimination, partial or complete, of crystal segregation or cored structure as discussed on pages 164 *ff*. The
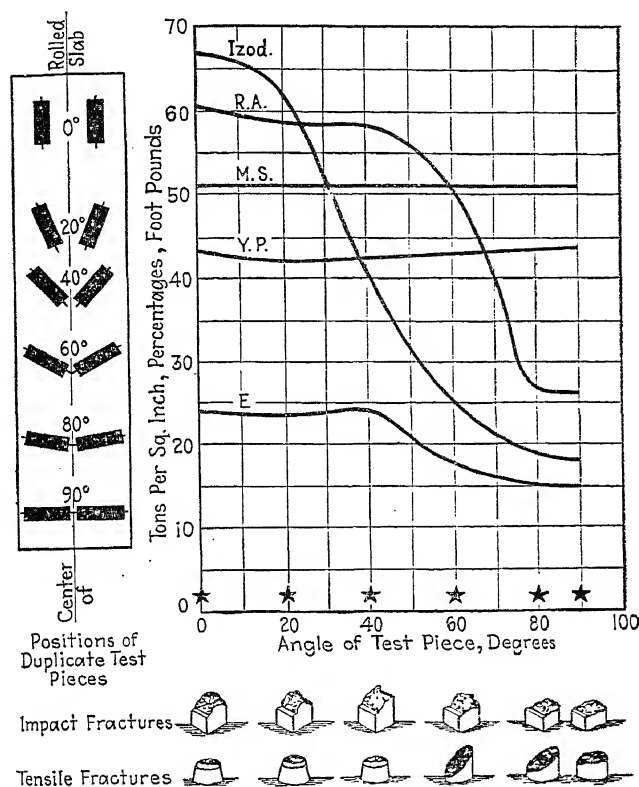
Fig. 105.—Influence of slag lines in Bessemer steel (0.23 C, 0.97 Mn, 3.08 Ni) on strength in various directions. (*Brearley.*)

properties of the hot-worked object are improved proportionally over those of a cast object. Ingot segregation is little altered, owing to the greater distances necessary for diffusion.

A hot-worked object, as for instance steel sheet, while it is usually stronger and more formable in the direction of rolling is less so in the transverse direction. The films and insoluble materials at the grain boundaries and within the grains, as

described on page 39, are rolled out into fibers (as the slag stringers in wrought iron) and form planes of weakness. Splitting takes place more readily parallel to these planes than at right angles to them. The two railway draw hooks in Fig. 104 have been etched to show the direction of these planes of weakness. The cracked one had, contrary to specification, been cut from a straight piece instead of being formed by bending. Figure 105 shows how tests made across the direction of rolling are much lower in impact (Izod), reduction of area, and elastic limit than are similar tests made parallel to this direction.

CREEP AND FATIGUE

Creep.—The amount of deformation in a metal specimen under a steady load below the elastic limit over a given period of time is proportional in general to the stress, the temperature, and the time during which the stress is borne. Such slow deformation is called *creep*. Since we have seen that polycrystalline objects possess no definite elastic limit, but have a limit depending upon the sensitivity of the measuring instrument, it is clear that these small stresses may lead to actual plastic deformation when sufficient time is allowed.

Probably the first recognition given to the industrial importance of creep was by Dickenson in 1922, when he published his researches on the creep resistance of structural-steel and alloy-steel members in a furnace. Since that time, the ever-rising operating temperatures of modern equipment and machinery—*e.g.*, high-pressure boilers, steam turbines, gasoline cracking stills, etc.—have led to many problems, among which are the failures of equipment under supposedly safe operating stresses. The result has been a more systematic attempt to investigate the reasons for creep, and even though the question has not yet been solved fundamentally, a mass of data, although not properly standardized, has been collected, and it is essential that some of the simpler aspects of creep be understood because of their engineering importance.

The application of a constant load to the specimen may result in a gradual deformation. The determining factors are the magnitude of the load and the time and temperature of its application. The *rate* of deformation may decrease with time, remain constant or increase with time, depending upon the inter-

working of the mechanisms of work hardening, recovery, and recrystallization, and the reduction of area due to the extension.

For the purpose of determining the suitability of a metal for a given use in which only a certain maximum distortion during the service life of the structure is permissible, tests on the creep resistance of the metal must be carried out. A typical creep curve is shown in Fig. 106. These tests determine the elongation at a given load and temperature for successive units of time. The curve may finally indicate creep at an increasing rate to fracture, as in *A*. It may show a constant creep rate, as in *B*, or
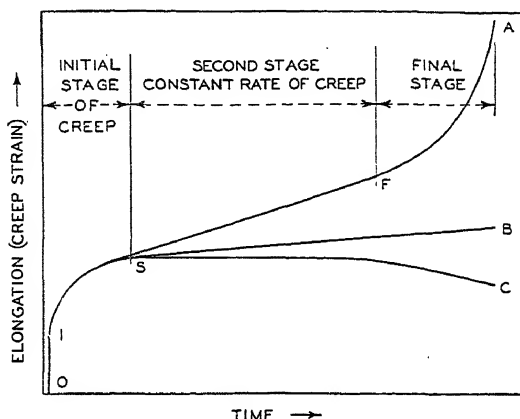
FIG. 106.—Diagrammatic creep curves illustrating the stages of creep, and the types of creep curves. (*Courtesy of Babcock and Wilcox Company and F. H. Norton.*)

a decreasing creep rate, as in *C*, depending on the duration of the test. Each test may be divided into three stages. The first stage is one of rapidly increasing creep rate following the original elastic extension in which slip and work hardening are taking place in the most favorably oriented grains, and a general redistribution of stress is taking place. This stage evidently is not indicative of the creep characteristics in the later stages. Stage 2, which indicates either a constant or a decreasing creep rate, is one evidently representing a balance between work hardening on the one hand and recovery and recrystallization on the other. Where the rate of work hardening is greater than the rate of recovery or recrystallization, creep proceeds at a decreasing rate, and stage 2 will be extended for a very long time.

Where the rate of work hardening just equals the rate of softening due to recovery or recrystallization, creep will proceed at a constant rate, and it is difficult to predict how long stage 2 will last. Where the rate of work hardening is less than the rate of softening, creep will proceed at an increasing rate and stage 3 will be rapidly entered. When the deformation becomes extensive in the second stage, the specimen necks down so that the load per unit area increases and stage 3 is entered, unless the rate of work hardening increases the resistance to deformation more rapidly than the reduction in area of the specimen increases the load. The simplest explanation of stage 3 seems to be that the rate of work hardening is less than the rate of softening, creep proceeds at an increasing rate leading to local necking, and the load increases until fracture takes place.

Although these relationships are undoubtedly the most basic conceptions of creep, there are so many influencing factors whose effect on these principles cannot yet be understood that eventually we may have to alter our stand. Such factors are grain size, stability of structure, composition, and as yet unsatisfactorily explained changes in the microstructure as creep proceeds. However, regardless of its fundamental explanation, the problem of creep must be recognized and dealt with from the standpoint of design limits. With the realization that a variation in operating temperatures of 10°F. may sometimes double the creep rate, and that specifications such as those demanded by turbine engineers that the stretch in turbine disks shall not be more than 0.2 per cent in a life of 25 years, or some 200,000 hours, the importance of the problem may be realized.

Fatigue.—The behavior of metals when they are subjected to alternating stress is extremely important in machine parts, bridges, and all structures subject to vibration. Such stresses may be direct (alternating tension and compression), torsional, bending, or impact stresses. Experimentation has shown that the repeated application of a stress may cause failure even when the stress is below the elastic limit of the material. Failure by such alternating stress is called *fatigue*. The maximum stress at which the material will operate indefinitely without failure is known as the *endurance limit*. When failure in such engineering members as axles, crankshafts, and floor beams of bridges occurs, the cause may almost invariably be attributed to fatigue.

The most commonly encountered type of alternating stress is that in which the maximum and minimum stresses are of equal magnitude but of opposite sign, *i.e.*, tension and compression. The testing machine designed to study such stresses is usually patterned after that of Wohler, one of the pioneer workers in this field. The machine employs a cylindrical cantilever specimen, which is rotated at its fixed end and weighted at its free end. The rotation subjects each point on the circumference of the specimen to a maximum in tension when that point is at the top of the specimen, and a maximum in compression when it is
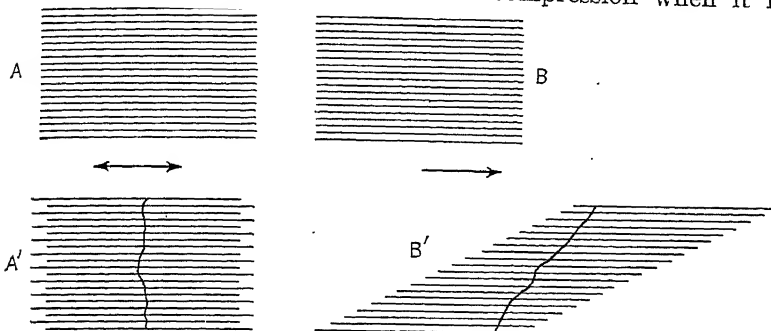
Fig. 107.—Schematic illustration of the deformation accompanying (a) alternating stress and (b) continuous stress. (*Courtesy of H. J. Gough and E. Benn, Ltd.*)

at the bottom of the specimen. When the point is at either side of the specimen, the stress is zero. The change in stress at each point is gradual and follows a sine curve.

When a plastic material is stressed in tension, the cross-sectional area contracts locally, forming a neck. Although the entire specimen elongates and work-hardens, the elongation and the work hardening occur *more rapidly* in the necked region than in the rest of the specimen. This occurs because the unit stress in the necked region is much higher than that outside it. Fracture occurs in this necked region. In fatigue, however, no appreciable general elongation occurs and no neck forms prior to fracture. Nevertheless, work hardening does occur. It remains to consider by what mechanism that work hardening takes place.

A stress cycle in fatigue involves a complete reversal of stress from a maximum in tension to a maximum in compression and back to a maximum in tension again. In a cycle, then, there are two stages in which small plastic deformations take place. In

going from zero stress to a maximum in tension, deformation in one direction will take place, while in going from zero to a maximum in compression, the deformation will be in the opposite direction. Consequently, at the completion of the cycle the deformations have balanced each other and the piece has the same external shape. However, the internal structure has been deformed and from that internal deformation the work hardening

As Received

Specimen unbroken

48,500 p.s.i.

Stress, Lb. per Sq. In.

60

50

40

10^6 10^7
Cycles to Failure
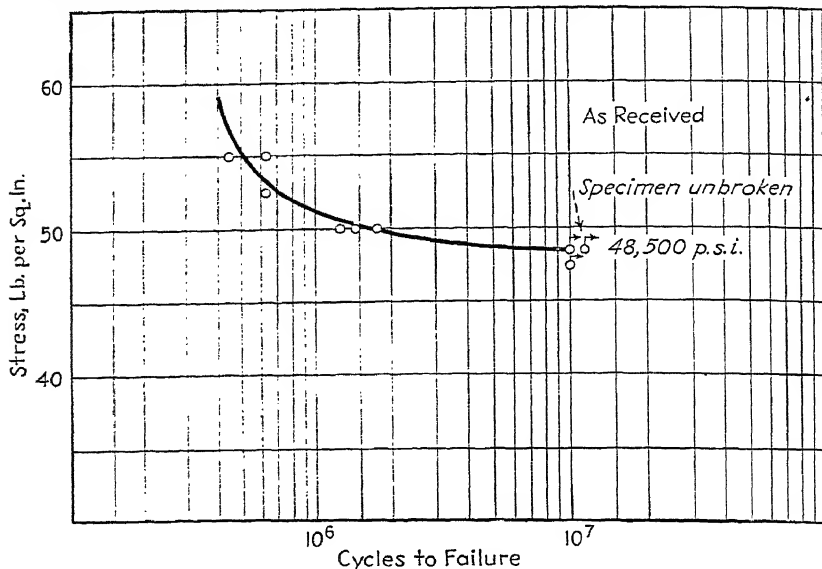
Fig. 108.—Typical S-N curve for steel.   (*Courtesy of C. M. Offenhauer.*)

arises. Figure 107*A* illustrates the block movement in ordinary crystal deformation. It resembles the deformed zinc single crystal on page 88 and results in a general elongation. Figure 107*B* illustrates the alternate and opposite block movement in crystal deformation by fatigue and no appreciable elongation results. Work hardening occurs in each case, regardless of the difference in change of shape.

In fatigue, as the alternate block movement within individual crystals proceeds, the specimen finally becomes so work-hardened that it can stand no further deformation and small cracks are formed, usually at the surface where the stress is the greatest. These cracks act as stress concentrators in the same manner as was discussed in relationship to the strength of metals, and with further cycles of stress, the cracks extend progressively into the

pecimen until the cross-sectional area is so diminished that the final fracture takes place suddenly.

Thus we see that work hardening is the fundamental mechanism by which a metal prepares for fracture and that the change of external shape is merely incidental to it.

Most metals possess an endurance limit, *i.e.*, a definite stress at and below which failure by fatigue apparently does not take place. When a series of stresses is plotted against the number of cycles to failure at each stress on a semilog scale, the curve evidently becomes perfectly horizontal at some particular stress. This stress is known as the *endurance limit*. A typical S/N curve, as it is called, is shown in Fig. 108. The number of cycles necessary to determine where the curve becomes horizontal varies for different metals. For steel, 10^7 cycles is considered satisfactory.

From a consideration of the mechanism by which a surface crack causes fracture in fatigue, the effect on the fatigue life of small surface imperfections such as pits or scratches can be realized. Such stress raisers would tend to reduce that life rapidly. Key slots, right-angle fillets, and other sharp changes in section in parts subjected to fatigue are dangerous.

Comparatively little work has been done on fatigue at elevated temperatures, but what results have been obtained show that as the temperature increases, the work hardening resulting from fatigue tends to be removed, *i.e.*, the metal is being hot-worked.

The recognition of the importance of fatigue has led to the periodic examination of essential parts of machinery, *e.g.*, airplane motor parts, axles, etc., to determine whether or not fatigue cracks have started in the parts examined. Investigations of this type serve to eliminate many dangerous and time-consuming accidents resulting from fatigue, and to indicate where the redesign of such parts would eliminate the cause for fatigue failure.

Elastic Aftereffect.—We have seen that if a polycrystalline material is stressed below its so-called *elastic limit*, it elongates gradually by creep. Upon removal of the load, the metal contracts along a line parallel to its original extension. If the original deformation was slight and if sufficient time is allowed, the metal will gradually return almost to its original length. This slow extension and contraction with time has been called the

aftereffect. The effect is probably not a purely elastic effect but a combination of both elastic and plastic effects. It may be visualized mechanically by a consideration that while a large mass of crystals unfavorably situated for slip may deform elastically at first load application, some few favorably situated crystals deform plastically. Now, if the load is removed soon enough, the tendency of the elastically deformed crystals to relieve their stress may be sufficient to cause an actual reverse plastic deformation in the plastically deformed crystals. Closely connected with this effect is the "Bauschinger effect," or elastic hysteresis.

Strain Aging.—In normal (undeformed) steel, if the stress is gradually raised until it passes the proportional limit, this limit if tested immediately afterward is higher than before the stress was applied. This result may be repeated. If, however, the stress is beyond the yield point, the proportional limit will sink and may reach zero. This condition is called *overstrain.* If deformed while in this labile condition, the metal will not show flow layers or "stretcher strains." If it is allowed to "age," *i.e.*, to lie at room temperature, or is heated in boiling water, the proportional limit returns to its original value or even above. This behavior is called *strain aging.* Stress above the original yield point removes this condition, but upon release of the stress the change may continue.

Similarly, stress above the original yield point lowers the modulus of elasticity, which returns, however, upon aging.

Stress beyond the original proportional limit in tension lowers the proportional limit in compression and vice versa.

The above characteristics apply to steel, and investigation of them will have to continue, perhaps for years, before adequate explanations are evolved. A knowledge of their existence is, however, of importance to engineers.

Summary of Deformation and Annealing.—In brief summary of the mechanical deformation and annealing of metals, we may say that the industrial forming operations produce amazing changes in the properties of the metals. The magnitude of these changes is different for the different properties. The greatest change occurs in the mechanical properties, including tensile and compressive strength, hardness, and resistance to bending. Less pronounced are the changes in permeability and

electric conductivity, and even smaller is the change in energy content and volume. The deformation of metals takes place principally by slip of fragments of each crystal past other fragments. Slip takes place according to certain crystallographic laws along certain crystallographic planes, and in certain directions on these planes. As slip proceeds, the frictional resistance to slip increases so that slip is self-stopping. This increase in friction may be attributed to a change in the atoms in the slip planes. There is very little change in the distances between the planes of atoms.

As deformation proceeds, the grains of the metal, originally oriented at random, gradually elongate and at the same time orient themselves in an orderly fashion with respect to the direction of flow, and a fiber structure develops in the metal.

The cold-worked condition is an unstable one, but it persists permanently at low temperatures. If the temperature is raised, recovery from this abnormal state begins and the physical and chemical properties begin gradually to return to normal. At higher temperatures the deformed structure gives way to a new generation of crystallites, small at first, but growing gradually in size.

At this stage the study of deformation may logically be linked with the industrial processes of rolling, forging, drawing, machining, and welding (see pages 289 to 306).

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PART II
METALLOGRAPHY

CHAPTER IV

THE STRUCTURES OF BINARY ALLOYS. THE PHASE RULE

The Importance of Alloys.—The internal structure and properties of pure metals have been studied in Part I. Profound changes in the properties of a pure metal may result if atoms of a second metal or atoms of a nonmetallic element are combined or alloyed with it. Both the physical and the chemical properties of the pure metal will be changed by the presence of the "foreign" atoms. The changes will be more marked in the crystalline state than in either the liquid or the vapor state. Such metallic combinations of two or more varieties of atoms are called *alloys*. Alloys are of great importance in industry and in the arts, in fact far more so, when quantitatively considered, than are the pure metals. The steels, the brasses and bronzes, aluminum alloys, bearing metals, and cast iron recall at once the importance of this class. Pure metals are desired for certain purposes, such as copper and aluminum for electrical conduction, and aluminum, iron, zinc, and tin for corrosion resistance. But far greater quantities of these metals are used in the form of alloys with other metals and even with small proportions of nonmetals, such as carbon, nitrogen, sulphur, and oxygen. It is the purpose of this chapter to develop a system, usually called *metallography*, for predicting in advance of its preparation in the laboratory what will be the normal internal structure of any certain alloy. And when its structure is known, then its properties, both physical and chemical, can be predicted, for out of the internal structure of an alloy arise its properties. It is for this reason that one is interested in internal structure. Clearly, knowledge of such a system will be of great usefulness in adapting metals to human use.

The foundation of this entire chapter is the great generalization of the American scientist, J. Willard Gibbs, called the *phase rule*. In order to keep the attention focused upon the usefulness of this

rule, rather than upon its mathematical origin, derivation of it is delayed, however, until the end of the chapter.

"Impurities" in Metals.—Even if the alloy is to be composed of only two metals, or of one metal and one nonmetal, these two may be combined in an infinite variety of proportions one to the other. In one instance a minute quantity of the one element, say 0.01 per cent, may be combined with 99.99 per cent of the principal metal, such as a trace of nickel in purified copper. In this case the minor metal may be termed an *impurity* in the major metal. In another instance the proportions may be 50 per cent of each metal, as in some of the commercial nickel-copper alloys; or the proportions may be anywhere between these two extremes.

Whether or not the presence of the foreign atoms in the alloy is intentional does not, of course, alter in the least their effects, either beneficial or deleterious, although the magnitude of the effects naturally may be less when the proportion of foreign atoms is small.[1] In some cases, however, as little as 0.01 per cent of a second element may change profoundly the corrosion resistance, the electrical conductivity, the magnetic permeability, or even the mechanical properties of the major metal. Oxygen-free copper seems to have remarkable toughness in the twisting test. Yet it differs from ordinary copper only by omitting the 0.03 to 0.08 per cent of oxygen. A few hundredths of a per cent of calcium in lead very greatly increases the strength, hardness, and endurance limit of the metal. Zinc is much affected by small amounts of cadmium and tin. Gold containing as little as 0.005 per cent Pb is unworkable owing to a eutectic at the grain boundaries. Bismuth in copper produces a network around the copper grains if 0.002 per cent bismuth is present. If more than 0.05 per cent bismuth is present, the copper cannot be cold-rolled. 0.01 per cent carbon in iron alters profoundly its magnetic properties. 0.01 per cent sulphur in nickel or 0.02 per cent sulphur in monel metal renders them so brittle that they fly to pieces if struck. 0.000,000,13 per cent HCN poisons platinum sponge as a catalyst. The striking "diseases" and "abnormalities" of metals that have attracted so much superstitious

s, "Impurities in Metals," John Wiley & Sons, Inc., New York, 1930.

attention in the past are, of course, merely instances in which our knowledge of the internal structure of the metals is incomplete.

The Structure Changes With the Temperature.—If the internal structure of each of the many alloys possible between two given metals had to be described, both as to number of phases and as to the composition and mechanical arrangement of each phase after cooling to room temperature, it would involve very lengthy descriptions or tabulations. If the structure of each alloy changed with the temperature, as it usually does, and if the structure above and below room temperature were wanted also, the tabulation would be impossible to carry out practically. Fortunately all these descriptions can be incorporated in a simple diagram after the exploration of an alloy system has been properly carried out. Most of the solubility limits of the possible binary diagrams have been obtained by the method of thermal analysis ("cooling curves" of alloys). More recently the changes in volume, in electrical conductivity, or in lattice form or dimensions have been used. The experimental methods for their determination will not be given in this text. Obviously, however, it will be essential for those interested in the best treatment and use of alloys to learn to read and interpret the known diagrams of this kind.

The general law which is expressed in all such constitutional diagrams, for, although very diverse in appearance, all such diagrams do conform to a general law, is called *Gibbs's phase rule.* This rule prescribes the number of phases (in the case of a solidified alloy it is the number of kinds of crystalline grains) that may be present in a given alloy when it is at a given temperature and pressure. The rule assumes that the alloy is in complete equilibrium with its environment at this temperature and pressure and has, therefore, no tendency whatever to change its condition, however long a time may elapse. Such equilibrium is frequently achieved in metallurgical practice by a complete, or "dead," annealing. The mechanical arrangement of these phases[1] with respect to each other also can be inferred from the diagram.

The Constitutional Diagram.—The base line or abscissa of the constitutional diagram in which these descriptions are contained shows the compositions of all possible alloys from 0 per cent of one metal and 100 per cent of the other metal at one end of the

[1] For a definition of the term *phase,* see p. 195.

line to 100 per cent of the one metal and 0 per cent of the other at the other end of the line, for any two metals or nonmetallic components. It is thus possible to represent any binary alloy by a point on this scale intermediate between its two extremes, as, for instance, 81 per cent of one component and 19 per cent of the other component, etc., as shown at x in Fig. 109. The vertical scale of the diagram represents the temperature range. Any point within the confines of the diagram as n, f, g, or x will therefore represent a particular alloy composition at a particular temperature.
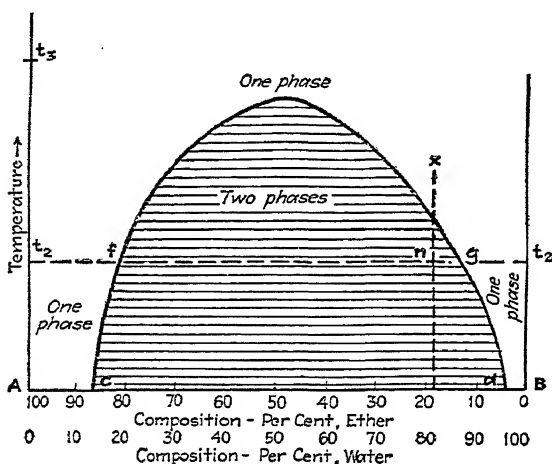
Fig. 109.—Hypothetical solubilities of ether and water for each other.

Solubility as Shown by the Constitutional Diagram.—If such a diagram is to show completely the internal structure of all possible alloys formed between two components, it must show, first of all, how much of one component will dissolve in the other when mixed, *i.e.*, it must show the *solubility* of one component in the other. For certainly the character of the alloy will be different if, for example, the added element dissolves in the crystals of the host metal from what it would be if the additions were insoluble in the host crystals. The heat-treatment of steel and the aging of duralumin depend entirely upon the changes in solubility of alloying elements in the iron and aluminum with change in temperature. Not only the mechanical properties, but also the chemical and physical behavior, such as corrosion resistance and electrical and mechanical properties, change,

often abruptly, with changes in solubility of the components of the alloy.

Theoretically every metal can dissolve at least a trace of every other element, complete insolubility being thermodynamically impossible, but there are some metals that can dissolve large proportions of others, and frequently two metals are soluble in all proportions in each other, both when liquid and when solidified. A familiar analogy is the complete solubility of alcohol and water in all proportions. Ether and water, on the contrary, if shaken up in a test tube will not dissolve completely but will separate into two layers (two "phases"), the upper layer being, however, as a little thinking will convince one, not pure ether but ether saturated with water, and the lower layer not pure water but water saturated with ether. Increasing the *amount* of ether or water does not change the *concentration* of the two layers, or phases, at least not until so much water (or ether) has finally been added that it dissolves all the other component and is thereby left unsaturated. Each will remain saturated in the other as long as the layers are in contact and free to diffuse, and merely the quantity of each phase may change. Oil and water may represent the other extreme in which the two components are substantially insoluble in each other. Comparatively few metals exhibit such immiscible layers in the liquid state. Copper and lead, and zinc and lead (Parkes process) are examples of metals, however, that separate, even when liquid, into two layers, each layer containing very little of the other metal in solution. Metal pairs that are insoluble in the liquid state will not be considered further in this chapter, for such pairs are usually held to be incapable of forming alloys. The alcohol-water, ether-water, and oil-water analogues cited above will, therefore, be used here to represent the solubilities of *solidified* metal pairs only.

The constitutional diagram is a plot of these solubility relations and shows, therefore, the number and composition of crystalline or liquid phases present in any alloy at any temperature.

A change in the pressure on a system will change the solubility relationship just as a change in temperature will, but, since the effect of pressure on alloy systems is only beginning to receive study (most of the treatment of metals being done at atmospheric pressure), usually the pressure axis of the diagram is not shown, because pressure has a minor effect on alloy equilibria. The

complete diagram—pressure-temperature-volume (or its recipro-
cal, concentration[1]) for a one-component system—water—is
shown in Fig. 2 on page 13.

Two Rules for Interpreting Constitutional Diagrams.—Let the
distance *Ac* on the hypothetical diagram of Fig. 109, chosen for
simplicity, show that at 0°C. ether dissolves *c* per cent of water,
i.e., about 13 per cent of water (measured on the water composi-
tion scale below *c*). Water at this temperature then appears to
dissolve *d* per cent of ether, *i.e.*, about 4 per cent of ether (meas-
ured on the ether scale below *d*). At a higher temperature, as at
t_2, the distance *Ac* has increased to t_2f, showing an increased
solubility of water in ether to about 18 per cent, which is natural
to expect at the higher temperature. An increase has taken
place also in the solubility of ether in water (distance *Bd* to t_2g)
to about 13 per cent owing to the rise in temperature. The
increase in solubility need not be the same for the two and, in
fact, usually is not so. At a still higher temperature, t_3, the two
liquids are completely soluble in each other in all proportions,
as is shown by the meeting of the two lines. Separate layers of
ether and water phases could not exist when equilibrium has been
reached at this higher temperature. The line *cf* (continued)
thus shows the changing solubility-limit of water in ether, and the
line *dg* (continued) the changing solubility-limit of ether in
water, as the temperature changes. The area between these
lines is a region in which saturation is exceeded and two phases
exist, namely, an ether solution saturated with water and a water
solution saturated with ether, in contact with each other.[2]

Rule 1. To ascertain the composition of the water layer and
of the ether layer, when both are present (which is possible by
choosing certain total compositions) at any chosen temperature
below t_3, one needs only to *draw a horizontal exploring line at the
chosen temperature. The intersections of this line with the two
boundaries of the two-phase (shaded) field give (by projection upon*

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[1] The volume of unit weight is expressed in cubic centimeters, whereas
concentration is expressed in grams per cubic centimeter.

[2] A lecture table experiment which illustrates clearly these changes of
solubility with change in temperature is the heating in a Bunsen flame of
a test tube containing equal parts of water and phenol. Two layers form at
room temperature. They dissolve completely at 68°C., and separate again
into two layers on cooling. The layers may be colored red with eosin.

the abscissa) the compositions of each of the two phases existing at that temperature. For instance, at temperature t_2 the ether phase will contain f per cent water, the water phase g per cent ether. If the original total composition lies outside the shaded area only one phase is present, being unsaturated, and its composition is, of course, the same as the original total composition of the

p

Rule 2. Not only is the composition of each of the two phases that can be present at any temperature shown by this diagram but also the relative *quantity* of each of these two phases present in any chosen original composition is given. To determine the quantity of each phase, it is necessary only to *erect a vertical line at the point on the composition scale corresponding to the total composition of the mixture as point n in the example above. The point where this vertical line intersects the chosen temperature horizontal line t_2, may be considered the fulcrum of a lever system. The relative lengths of the lever arms ng and nf multiplied by the amounts of the phases present must balance.* For example, in a composition of 81 per cent water and 19 per cent ether, as shown at x on the diagram, there will be present in the alloy at temperature t_2,

$$\frac{ng}{fg} \times 100 \text{ per cent of phase } f$$

and

$$\frac{nf}{fg} \times 100 \text{ per cent of phase } g$$

For, clearly, if the point n lay midway between f and g, there would be 50 per cent of each phase present, while if n lay at the point g, there would be none of phase f present. The lengths ng, fg, etc., are read from the composition base line. A little consideration of these conditions will make these relations quite obvious. The compositions of each of these two phases, f and g, are known from Rule 1 given in the paragraph above.

These two rules thus give both the composition of each phase and the relative quantity of each of the two phases present in any binary system, whether these phases be two liquids as in the case of ether and water, or two varieties of crystals in a solidified alloy, such as cementite and ferrite in steel, or whether they be one liquid phase and one solid phase, as in the pasty stage of a

partly solidified alloy. *They are the only two rules necessary in evaluating diagrams of binary alloys.*[1]

Complete Solid Insolubility. The Eutectic Reaction.—By virtue of showing the temperature at which separation of a second phase takes place from a solution, the diagram thus shows the temperature of *freezing* of that solution, *i.e.*, it shows the temperature of separation of a crystal phase from a liquid phase. Let us consider first the simplest case, in which two substances are completely soluble in each other in the liquid state but completely insoluble in each other in the crystalline s t a t e. Raoult's law states that the freezing point of a pure substance will be lowered by the addition of a second substance (provided the latter is soluble in the pure substance while liquid and insoluble in it when solidified), the amount of lowering being proportional to the molecular weight of the solute. For an alloy of Raoult's type, namely, one showing complete solubility of the two components in each other when liquid and complete insolubility when solid, the diagram shows a freezing-point curve beginning at the freezing point of the pure metal and dropping steadily with each addition of the second substance, as shown in Fig. 110. This curve is a straight line in the region of dilute solution. It indicates the temperature at which freezing begins for each alloy and

FIG. 110.—Change of freezing point of liquid A when B is added to, or A crystals are precipitated from, solution.

[1] HOYT, "Metallography." Part I: Principles, McGraw-Hill Book Company, Inc., New York, 1921.

RUER-MATHEWSON, "The Elements of Metallography," John Wiley & Sons, Inc., New York, 1909.

RIVETT, "The Phase Rule," Oxford University Press, New York, 1923.

WILLIAMS and HOMERBERG, "Principles of Metallography," McGraw-Hill Book Company, Inc., New York, 1939.

it is called the *liquidus* line. In the region above it the alloy is entirely liquid. This upper region is, therefore, a one-phase field and is not shaded. Immediately below the liquidus, the melt has begun to form solid crystals. Therefore, the region below the curve is a two-phase field containing one liquid and one crystalline phase (instead of two liquid phases as in the ether-water analogue in the example of Fig. 109) and is shaded as is done also in the two-phase field in Fig. 109. The quantity and composition of each of these two phases, one liquid and one crystalline, for any alloy at any temperature may be found by the two rules used just as they were used in interpreting Fig. 109. For example, in Fig. 110 suppose that an alloy 90 *A* 10 *B* is a homogeneous liquid solution *x* of two metals *A* and *B*, instead of ether and water. As its temperature falls on cooling and crosses the liquidus curve at *x'*, the liquid begins to deposit crystals (not, it will be noted, at the freezing point of pure *A* but below in accordance with Raoult's law) by the formation of nuclei, as described in Chap. I. Since metal *A* when solid is *assumed* to have no solubility whatever for *B*, it is obvious that the crystals of *A* deposited can contain no *B*, but must be pure *A*. The broken horizontal line drawn at the point where *x'* cuts the liquidus shows correctly, therefore, that the crystalline phase has composition 100 per cent *A*, the liquid phase composition *x'* (Rule 1). If the melt were transparent, it would reveal at this time crystals of pure *A* swimming in a liquid of composition *x'*. This loss of pure *A* material by deposition from the liquid must impoverish the liquid in *A* and thus leave it richer in *B*. This new liquid, richer in *B*, has a lower freezing point than the *x* liquid, (just as it would have, if we were to start with it instead of with the liquid *x* in our experiment). No further deposition of crystals from this liquid can take place, therefore, until its temperature has dropped slightly, when the deposition of pure *A* crystals will be resumed. These processes continue, the amount of the crystalline phase (pure *A*) increasing gradually by continued precipitation of *A* from the liquid, the liquid phase gradually decreasing in amount and traveling downward and to the right along the liquidus curve, constantly becoming richer in *B* content and falling in temperature. At any temperature t_1, the per cent of the crystalline phase (pure *A* crystals), will be $np/op \times 100$. That of the liquid phase (of composition *p*) will

be *on/op* $\times$ 100, as was shown for the conventionalized ether-water diagram in Fig. 109.

Let us leave, for a moment, this side of the diagram and consider what would happen to an alloy nearer the *B* side, say, 80 per cent *B*. The conditions are shown in Fig. 111.

Again the liquidus curve droops from the freezing point of pure *B*, owing to increase in the amount of *A* present in the melt according to Raoult's law. The crystals deposited from this melt *y* containing 80 per cent of *B*, are pure *B* in accordance with our *assumption* of complete insolubility of each component in the other after solidification. The melt becomes richer in *A* as a result and falls in temperature, moving downward and to the left along the liquidus. The conditions might be stated by saying that whereas alloy *x* was saturated with *A* on cooling below the liquidus, and deposited pure *A* crystals, alloy *y* is saturated with *B* on cooling below the liquidus, and deposits pure *B* crystals. At temperature t_1 alloy *y* will consist of $ht_1/kt_1 \times 100$ per cent of liquid (of composition *k*), and $kh/kt_1 \times 100$ per cent by weight of crystalline material of composition t_1, *i.e.*, of pure *B*.

Fig. 111.—Change of freezing point of liquid *B* when *A* is added to, or *B* crystals are removed from, solution.

The two liquidus curves, the one dropping from *A* and the one dropping from *B*, meet and intersect somewhere between *A* and *B*, as shown at *e* in Fig. 112. Clearly, the liquid once arrived at this point of intersection *e* might have approached it either from the *A* side or from the *B* side of the diagram; *i.e.*, previous to its arrival at this point, it might have been saturated in either *A* or *B* material, depending on what composition had been chosen originally. At this point of intersection it is obviously saturated in *both* kinds of material and must, therefore, precipitate both kinds of crystals. The result is that it now precipitates *alternately* a crystal of *A* and one of *B* at various points in the remaining liquid, as fast as the heat set free by crystallization can be

carried away, until solidification is complete, the temperature and the composition of all three phases (melt, A crystals, and B crystals) remaining constant and unchanged during the process.[1] At any locality in the melt where an A crystal is precipitated the surrounding liquid is left supersaturated in B material and a B crystal precipitates next to the A. Such an
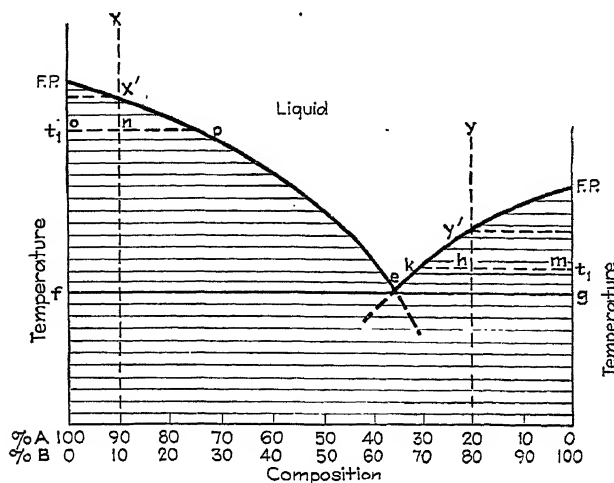
FIG. 112.—The eutectic reaction. Liquid α precipitates crystals of f (pure A) alternately with crystals of g (pure B).

intersection of liquidus curves is known as a *eutectic point*. The dissociation of the eutectic liquid of composition e into crystals of A and B is known as the *eutectic reaction* and may be written

$$\text{Liquid } e \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \text{ crystals } A + \text{crystals } B$$
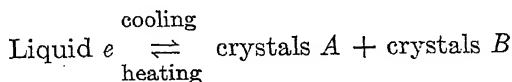
Since solidification is complete for all alloys at this temperature, a horizontal line fg is drawn at this level across the entire diagram. This line is called the solidus line, or the *solidus*.

The Structures of Eutectic Alloys.—The *micro*structure (for the structure is usually so fine that the aid of the microscope is necessary to reveal it, although in some instances the *macro*-structure, which is visible to the naked eye, may be significant) of alloy x in Fig. 112 is now simple to predict. It will show crystals of pure A which have come out in the earlier stages of

[1] See phase rule application for this case, p. 196.

freezing, prior to reaching the eutectic point, and grown to considerable size, so-called *primary* crystals of *A*, surrounded by alternate, smaller crystals (since each has had less time to grow) of *A* and *B* in a finely divided eutectic matrix or background (shown diagrammatically second from the left in the bottom row of structures in Fig. 113, also shown third from the top in the left-hand column of structures in this figure).   The primary *A* crystals might resemble the pebbles in concrete.   Both the large
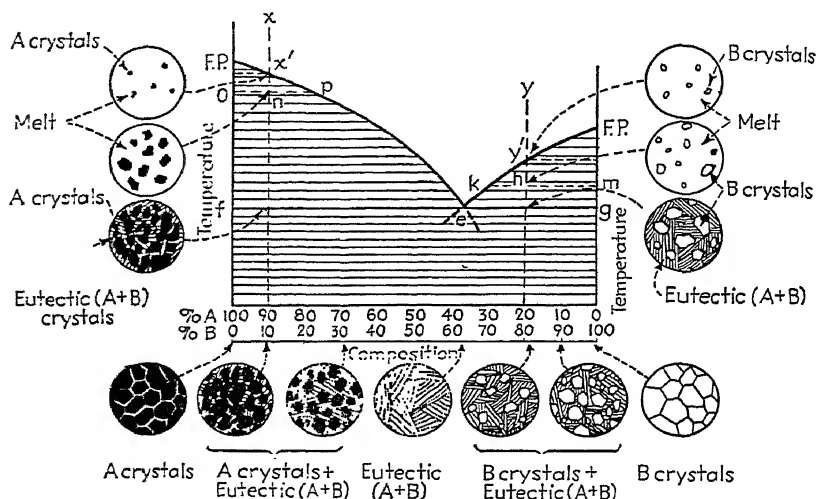
Fig. 113.—The structure of *x* and *y* alloys during solidification, and of other alloys at room temperature.

and the small *A* crystallites as well as the small *B* crystallites will be pure in accordance with our assumption of complete insolubility in the solid state.   A structure containing two crystalline varieties, as this one does, is called a *duplex* structure.   Thus we see how a reading of the diagram of Fig. 112 enables one to predict the structure of any given alloy, both during its cooling and after it has reached room temperature.

The appearance of these two alloys, *x* and *y*, at successive stages during the cooling of each is shown at the left and right sides of Fig. 113.   At the bottom of the diagram are shown the structures of several other alloys between pure *A* and *B*, when slowly cooled to room temperature.   It will be noticed that the proportion of *primary A* crystallites increases from zero at the eutectic composition toward 100 per cent at the pure *A* ordinate,

while that of primary *B* increases from zero for the eutectic alloy toward 100 per cent for an alloy of pure *B*.[1]

Now we may consider an actual alloy diagram. The simplified constitutional diagram of the alloys of aluminum and silicon is shown in Fig. 114, neglecting the important but slight solubility of
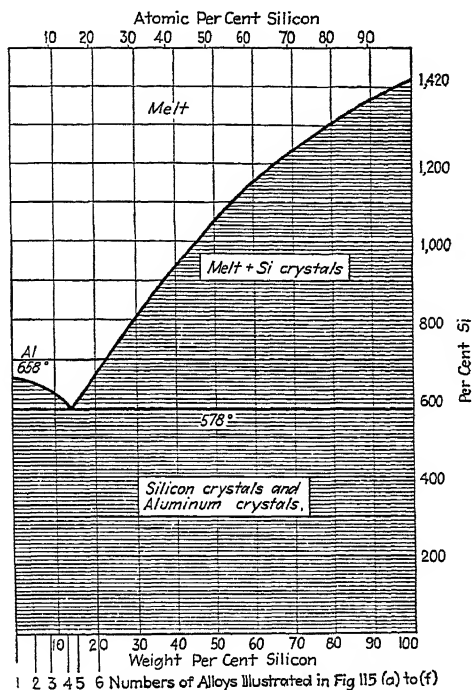
Fig. 114.—Simplified constitutional diagram of aluminum-silicon alloys.

silicon in crystals of aluminum. Beginning at the left of the diagram with alloy 1, as listed at the bottom of Fig. 114, we have the microstructure[2] of pure aluminum shown in Fig. 115a. Even the boundaries of the pure aluminum grains are scarcely discernible. Alloy 2 of Fig. 114 shows at 115b dendritic grains of aluminum surrounded by eutectic of small grains of aluminum

[1] The proportion of eutectic present is, of course, 100 per cent for an alloy *e*; 0 per cent for pure *A* or pure *B* and inversely proportional as the distance between *f* and *e*, and between *e* and *g*, as given by the second rule.

[2] For laboratory methods of polishing and etching metal specimens for examination of their structures see literature references at end of chapter, particularly the "National Metals Handbook," 1939 ed.

(a) Alloy 1   99.97 % Al

(b) Alloy 2   Si 4 %

(c) Alloy 3   Si 8 %

(d) Alloy 4   Si 12 %

(e) Alloy 5   Si 14 %

(f) Alloy 6   Si 20 %
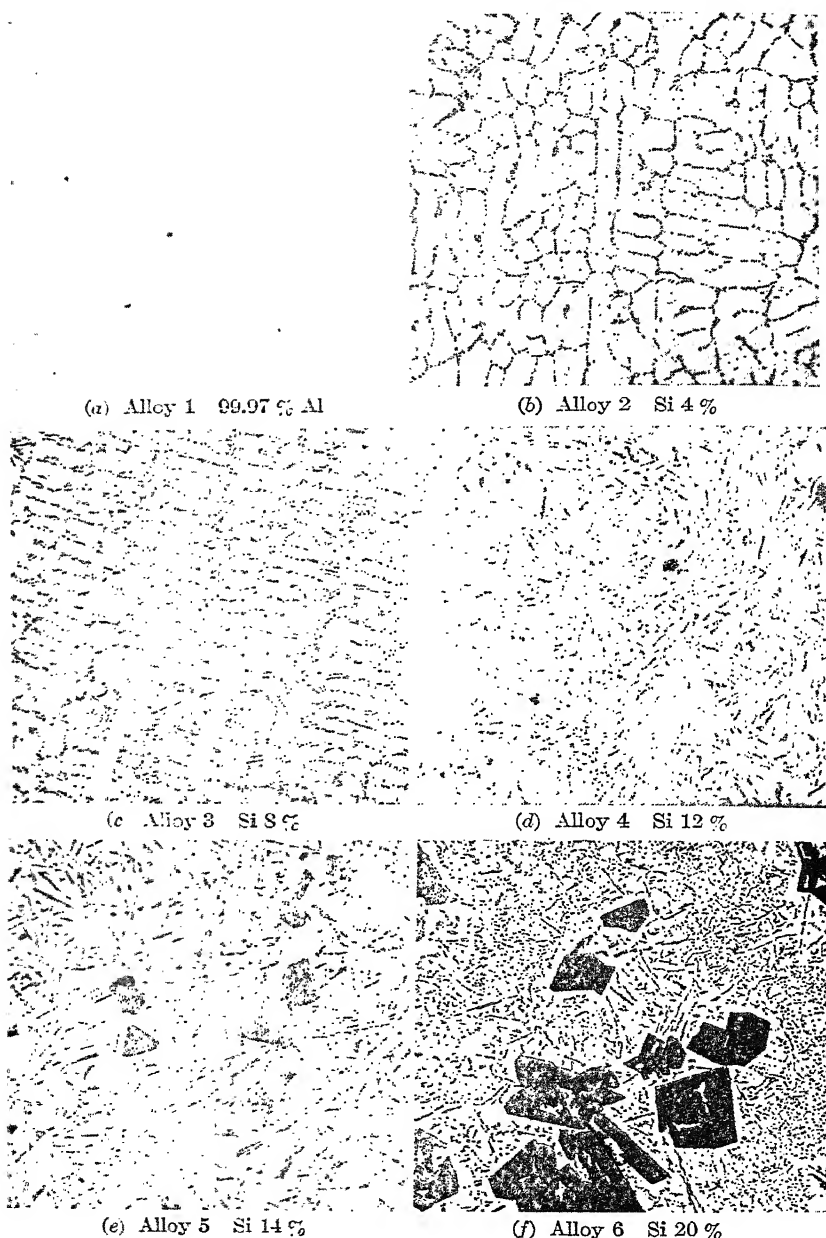
FIG. 115.—The structures of aluminum-silicon alloys, as numbered at the bottom of Fig. 114.   (*Courtesy of the Research Laboratory, Aluminum Company of America.*)

and silicon. In Fig. 115c the eutectic increases and in d it occupies the entire field. In Fig. 115e primary silicon grains appear, set in the same aluminum-silicon eutectic and in f the proportion of primary silicon increases. From a diagram of this type, it is thus possible to predict the amount of primary crystals

(a) Alloy 1 Sb 5 %   (b) Alloy 2 Sb 10 %   (c) Alloy 3 Sb 13 %

(d) Alloy 4 Sb 20 %   (e) Alloy 5 Sb 30 %   (f) Pb-Sb Diagram
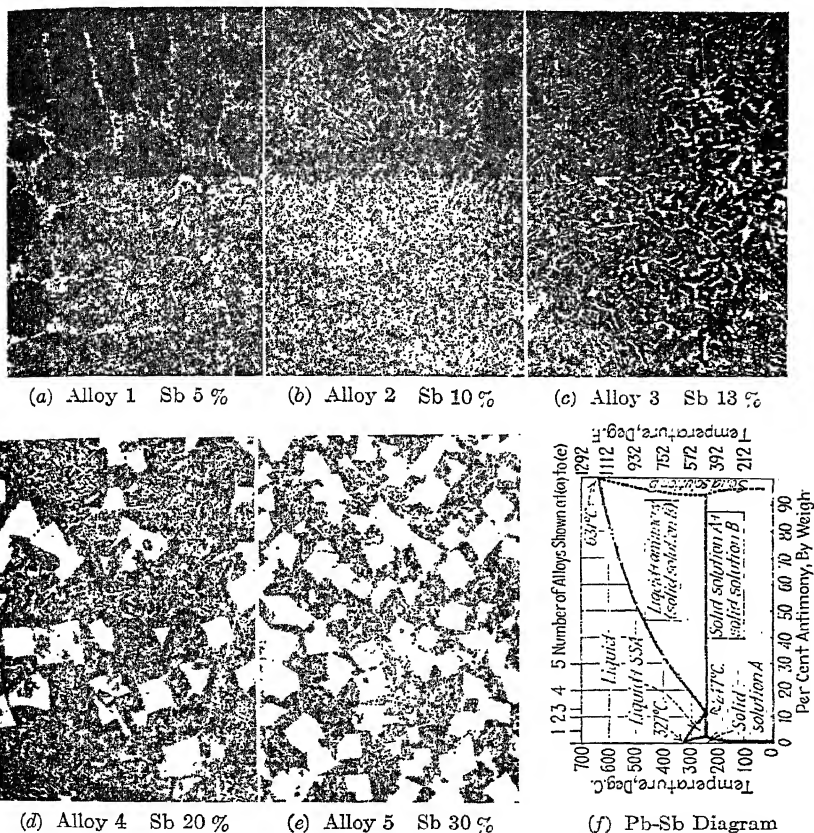
FIG. 116.—The structures and diagram of lead-antimony alloys (white = antimony, black = lead). (*Courtesy of Mr. M. H. Folkner.*)

of silicon or aluminum, and the amount of the eutectic that the alloy will possess after solidification. It foretells the temperature of initial freezing, the proportions of liquid and crystals during freezing, the composition of each phase, and the temperature of complete solidification (in this case the eutectic temperature) for every alloy of the series. To test the two rules given above

in this system aluminum-silicon, solve Metallography Problem 1, page 192.

In some abnormal eutectic alloys "primary" crystallites of one metal are formed with encasements of the other metal around them. Tammann has pointed out that the encasements are not due to supersaturation but to slow diffusion.[1] Figure 116 shows the structures of another eutectic system: lead-antimony. The slight solid solubilities may be neglected at this time. The student should locate each alloy (5 per cent Sb, 10 per cent Sb, etc.) on the diagram and correlate the structure given. Note the encasements of lead (black) around the primary (white) antimony crystals in d and e.

Cooling Curves of Eutectic Alloys.—The time-temperature or cooling curve of alloy x (Fig. 113) would show a change in slope at x, as seen in Fig. 117, owing to the evolution of heat accompanying the separation of A crystals. The curve, however, would not be horizontal at this point because, as has been pointed out, the temperature of the melt falls constantly as A crystals separate. When the eutectic separates at temperature f, the line becomes horizontal, because the composition of the melt remains constant and unchanged in proportion of A and B. (See phase rule application of this case on page 197.) The graph for alloy y would be similar. The cooling curve for alloy e, Fig. 113, would show no change in slope until the horizontal at temperature f is reached.

FIG. 117.—Time-temperature curve for alloy x, Fig. 113.

Complete Solid Solubility.—The eutectic reaction just described was based on Raoult's condition of complete solubility in the liquid state, complete insolubility in the solid state. It occurs in a large number of important alloy systems, usually, however, in a slightly modified form in which each of the two kinds of crystal that separate from the melt is not quite pure but contains a little of the other metal in solution, as will be explained on page 168.

[1] *Z. anorg. Chem.*, **210**, (2), 166, 1933.

Equally important with the above case of assumed complete insolubility of two metals in the crystalline state is the opposite case, namely, that of complete solubility. For this case one would expect, at first thought, that the liquid, whatever its composition, would simply deposit crystals of the same composition as the liquid, and thus solidify as a pure metal does. While very special alloys do solidify in this manner, they are relatively
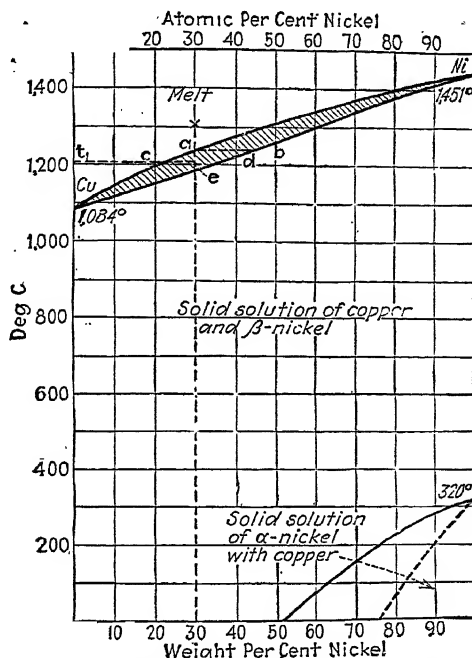
FIG. 118.—Constitutional diagram of copper-nickel alloys.

rare. Most of the completely soluble alloys deposit crystals that show a measured degree of difference in composition from that of the liquid in which they grow. A familiar example of a similar case is the distillation of a water-alcohol solution. The distillate is usually richer in alcohol than was the original liquid, although alcohol and water are completely soluble in all proportions in both the liquid and vapor states.

The freezing point of the pure metal may be either raised or lowered, in this case of complete solubility by the addition of foreign atoms, since it does not come within the scope of Raoult's

law.[1] A typical diagram, that of copper-nickel, will appear as in Fig. 118 in which the freezing point of copper is raised, while that of nickel is lowered. In this case of complete solubility the freezing points of the alloys fall constantly as the proportion of copper in them increases. The upper line connecting the freezing points of pure copper and nickel is the liquidus curve at which crystallization begins in the cooling of each alloy. The lower line is the solidus, at which crystallization is complete. The
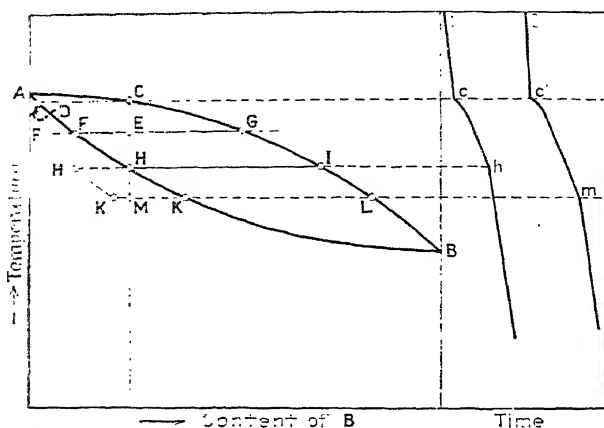
Fig. 119.—Effect of incomplete diffusion during freezing, on the position of the solidus line. (*Goerens.*)

enclosed area is a two-phase field of one liquid and one crystalline phase.

Solidification of a liquid alloy of this type consists of two processes:

1. Formation and growth of crystals in the melt.
2. Homogenization of the composition in various parts of each crystal:
    a. By diffusion between core and encasement.
    b. By diffusion between core and melt.

If process 1 is more rapid than process 2, as is usually the case in industrial metallurgy, equilibrium will at no time exist between crystals and melt, and the solidification of the alloys will not follow the solidus line of the diagram exactly. Because this condition is important industrially, it will be described here.

The Solidification of Completely Soluble Alloys.—If a melt of composition *C* in Fig. 119 falls in temperature until it cuts the

[1] For a discussion of the theory involved, see p. 166.

liquidus AB, it will, according to Rule 1, precipitate crystals of composition D, shown in Fig. 120a. These crystals are richer in A than the melt, hence their separation leaves the melt richer in B. They are not, however, pure A, it will be noted (see Fig. 119). A further fall in temperature to E causes the melt to precipitate crystals of composition F encasing the D crystal cores and also forming separate F crystals as in Fig. 120b. If equilibrium is to be established at this temperature, complete diffusion between the D cores and the F encasements of Fig. 120b must be accomplished. Also, in order that the entire composition of the crystalline phase may be brought up to that of the point F in the diagram, some B atoms must diffuse clear into the A-rich center
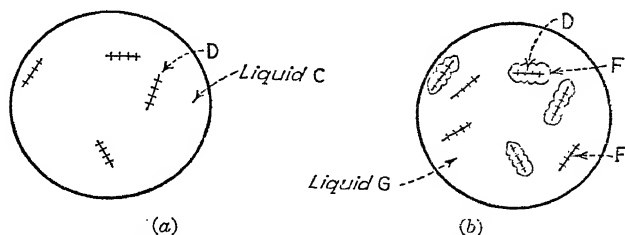
FIG. 120.—(a) Dendrites of composition D in Fig. 119; (b) encasements of F and dendrites of F in Fig. 119.

of the crystals from the liquid, for obviously a diffusion between D material and F material can result only in a composition intermediate between D and F and not in the composition F. Then, if diffusion keeps pace with crystal growth, the melt will move downward along the liquidus, and the crystals will move downward along the solidus in both temperature and composition as the alloy cools. If, on the contrary, diffusion lags, the crystals at temperature E will not be of homogeneous composition F, but will contain cores of D composition and encasements of F and will have an average composition as represented at F'. At temperature H, the average composition of the crystalline phase is not H but H'; *i.e.*, the crystalline phase is constantly richer in A material than it would be under equilibrium conditions.

Consequently, the melt must be greater in amount than it would be under equilibrium conditions and, rather than solidification being complete at H, there is still some liquid present. For illustrative purposes the amount of liquid may be considered as $HH'/H'I \times 100$ per cent. Further drop in temperature is

necessary to complete the solidification of this liquid. The precipitation that takes place as encasements on the crystals already formed follows the solidus from H to K, the average crystal composition following the hypothetical solidus $H'K'M$. Incomplete diffusion has had the effect, as shown on the cooling curves to the right of the diagram, of lowering the completion of freezing from temperature H down to temperature M.
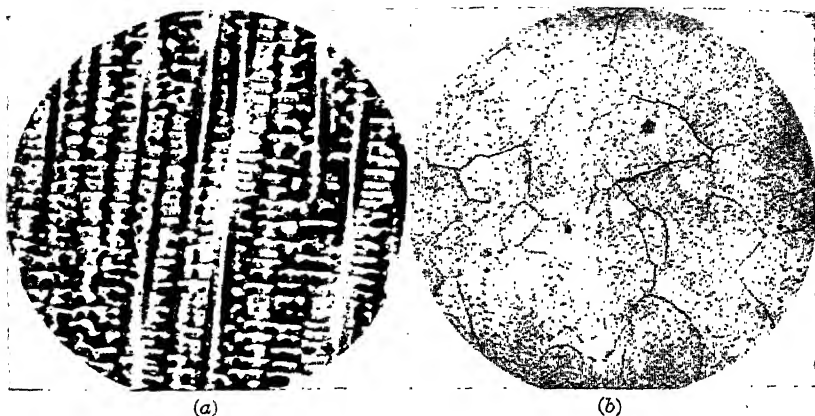
FIG. 121.—(a) Nickel-rich cores in a copper-nickel alloy before annealing; (b) homogeneous solid solution after annealing.   (*Evans.*)

While the progress of solidification has been described above as if it took place in abrupt steps, actually, of course, it is a continuous process, each deposit grading gradually from the previous one.

The Structures of These Alloys.—The appearance of the microstructure of a copper-nickel alloy (completely soluble, for constitutional diagram see Fig. 118) in this nonequilibrium condition is shown in Fig. 121a. The white dendrites or cores (D in Fig. 120) are richer in nickel than the black encasements (F in Fig. 120), which contain more copper. The reason for the abrupt boundary between white and black portions is that the etching acid attacks and blackens all nickel-copper alloys up to a certain limit of nickel content ("corrosion limit," as explained in Chap. VIII) and leaves the central cores, which are richer in nickel than this limit, unattacked. If the alloy in this condition is annealed for a long time just below the melting point, diffusion between the cores and encasements is completed and the micro-

structure of a homogeneous solid solution is obtained (Fig. 121*b*). Since we cannot see the individual atoms of nickel and copper in the crystal lattice, the grains appear like those of a pure metal.

Industrially this homogeneous condition is achieved not by a very slow cooling rate during solidification (which would result in very large grains, requiring a long time for diffusion from center to periphery to be completed) but by chill casting to give a fine grain size, followed by either severe cold deformation and annealing, or by hot deformation, to accelerate equalization by diffusion. Figures 122*a* and 122*b* show the initial and an intermediate stage

(*a*)

(*b*)
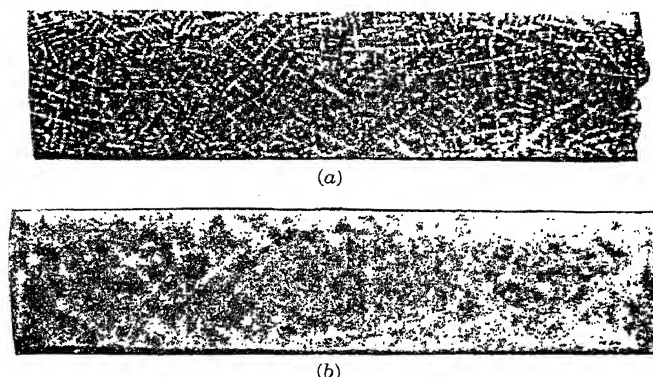
FIG. 122.—(*a*) Dendrites (nearly pure ferrite) in cast steel; (*b*) partial elimination of dendrites by diffusion. (*Oberhoffer.*)

of diffusion in a cored cast steel. When rolled out into sheets and shapes, these ferrite dendrites give rise to ferrite "bands." At room temperature the rate of diffusion in these "cored" crystallites is so slow that cast bronzes in the tombs of the kings in Egypt still show, after 4,000 years, this same nonuniformity. Many important industrial alloys, including the stainless steels, the gold-copper alloys, the simple steels, and others, are of this type as will be apparent in Fig. 256, page 341.

Quenching for the Solidus.—The true solidus line of alloys of this kind is not determined by the very slow cooling of a melt but rather by reheating specimens of a completely homogenized alloy to certain progressively higher temperatures and quenching one specimen drastically from each temperature. Examination of each quenched specimen will show one certain specimen in which melting had just begun at the grain boundaries before it was quenched. The specimen quenched from a temperature 5°C.

lower will show no such effects. The solidus for this alloy lies between the temperatures to which these two particular specimens were heated. Figure 272 shows the results of this method for the copper-beryllium alloys.[1]

To test the grasp of the diagram of completely soluble alloys, Problem 2, page 192, for the gold-platinum alloys should be solved at this point.

Rationale of Change of Melting Point.—The student may well ask how he is to understand the *rise* of melting point of a metal when a second metal is alloyed with it, since in the previous case, the simple eutectic, a *lowering* of the melting point always occurs. An explanation of the kind that follows makes this rise more rational and leads to a better understanding of the underlying cause of the rise.

First it will be necessary to prove that the vapor pressures of a crystalline phase and of its liquid are equal at the melting point. If this were not so, it would be possible to construct a closed U-shaped glass tube as shown in Fig. 123 with crystals C on one side and liquid l on the other, and this tube, if kept at constant temperature, would supply perpetual motion (Tammann), for the vapor pressures p and p_1 over the crystalline and the liquid phase, respectively, would be different pressures. By opening or closing the valve b the pressure change would move the piston a and any amount of energy desired could be extracted from the system. Since experience has shown that a perpetual-motion machine is impossible to construct, obviously p, the vapor pressure above the crystalline phase, must be equal to p_1, the vapor pressure over the liquid phase.

FIG. 123.—Proof of equality of vapor pressures at transition temperature. (*Tammann.*)

With this fact of the equality of vapor pressures at the melting point in mind, let us see how the addition of foreign atoms (a) to the liquid and (b) to the crystals would affect the vapor pressures of the two phases and, therefore, the melting point. Insoluble atoms have greater attraction for each other and draw off into

[1] The alloys in the α and β fields on page 362, of composition and temperature of quench marked with a cross, showed no evidence of incipient melting when examined. Those marked with circles did show such evidence.

two definite layers. If the foreign (solute) atoms are soluble in the liquid phase but insoluble in the crystalline phase, it is clear (1) that the attraction of native for foreign atoms must be greater than that of native atoms for themselves. Otherwise the two kinds of atoms would draw off alone and not dissolve. (2) This greater attraction certainly means that at the surface of the liquid, where the vapor forms by the escape of atoms from the surface of the liquid, fewer native atoms would escape per second and therefore (3) the vapor pressure of the liquid phase would be lowered. This lowering is

Fig. 124.—Lowering of the vapor pressure of a liquid A_0B_0 to AB and attendant lowering of the freezing point P_0 to N. (*After Müller-Pouillet.*)

shown from P_0 to N in Fig. 124. In this figure the curve A_0B_0 gives the vapor pressure of the pure liquid and C_0P_0 that of the pure solid. The point P_0 where the vapor pressures are equal
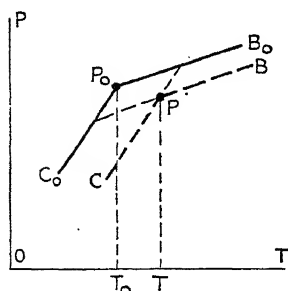
Fig. 125.—Lowering of vapor pressure of a liquid phase P_0B_0 to PB, and of a solid phase C_0P_0 to CP upon the formation of a solution, and the consequent *rise* of melting point.

must be the melting point. The curve AB shows how the vapor pressure of the liquid has been lowered by the addition of foreign atoms dissolved in it. The intersection of AB with C_0P_0 at N shows the melting point of the new solution. It has been lowered from T_0 to T. This completes the case for the lowering of melting point covered by Raoult's law. The vapor pressure of the solid phase C_0P_0 has remained unchanged because the foreign atoms cannot dissolve in it and therefore cannot influence its vapor pressure.

When the foreign atoms are dissolved in the crystalline phase *also*, it is clear that the vapor pressure of this phase will be lowered likewise. Depending on the relative degree of lowering in each phase, the melting point may either rise or fall. Thus, in Fig. 125 the temperature at which the vapor pressures are equal for the two *alloyed* phases is the point P, which

is a *higher* temperature than the point P_0.   The melting point has been raised.

This reasoning and result hold also for changes in phase other than melting as, for example, in polymorphic phase changes.

Partial Solid Solubility.—The two extreme types of alloys—those completely *insoluble* in the crystalline state and those completely *soluble*—have now been examined.   It remains to examine the very important intermediate type, which shows *partial* solubility in the solid state.   This requires the introduction of no new principles for its elucidation, but merely slight modifications of the extreme types already examined.   The lines *f*-F.P., *g*-F.P. in the eutectic system of Fig. 112 are merely curved slightly and moved a little closer to their corresponding liquidus curves, and two two-phase fields, resembling in form the more dilute regions of the two-phase field in Fig. 118, are obtained. The appearance is as shown in Fig. 126*a* (page 169).   The liquids in these alloys precipitate crystals that are never pure *A* or pure *B* but always contain a little of the other component in solid solution, similar to this extent to the completely soluble alloys.   In fact, near the points *FP* the diagram begins as if it would develop into the cigar-shaped diagram of a completely soluble alloy.   At the eutectic temperature the liquidi intersect, and the liquid precipitates alternately not crystals of pure *A* and *B*, as in the simple Raoult eutectic, but crystals of *A* containing *f* per cent of *B* in them, and crystals of *B* containing *g* per cent of *A*.   The rules for calculating the quantity of phases *f* and *g* are used just as before, as is also the rule for determining the amount of the eutectic matrix after complete solidification.   For example, alloy *z'* in Fig. 126*c* at temperature *fne* would contain *fn/fe* × 100 per cent of liquid (of composition *e*) and *ne/fe* × 100 per cent of crystals (of composition *f*).   At temperatures above the eutectic temperature the alloys behave just like the completely soluble type of Fig. 119, showing the cored structure if rapidly cooled.

Below the temperature of the eutectic line *feg*, a familiar phenomenon takes place.   As the temperature falls, there is a decrease of the solubility of *B* in crystals of *A*, and a decrease in the solubility of *A* in crystals of *B*.   If we attach the lines *fc* and *gd* of Fig. 109 shown in Fig. 126*b*, to the points *f* and *g* of Fig. 126*a*, we have the completion of Fig. 126*c*.   In this case the two phases between lines *fc* and *gd* are two *solid* phases instead of
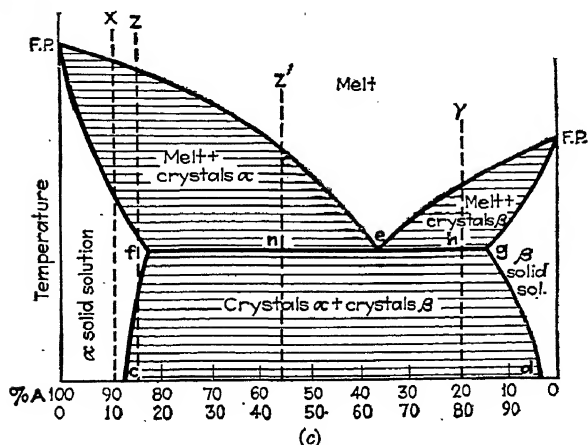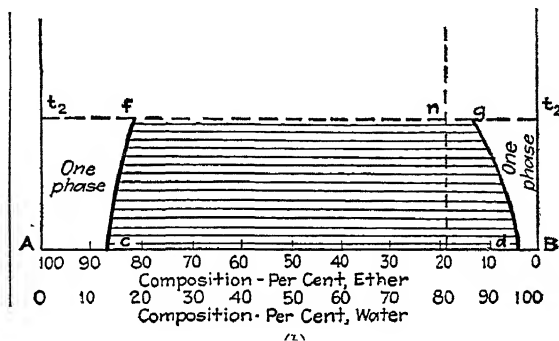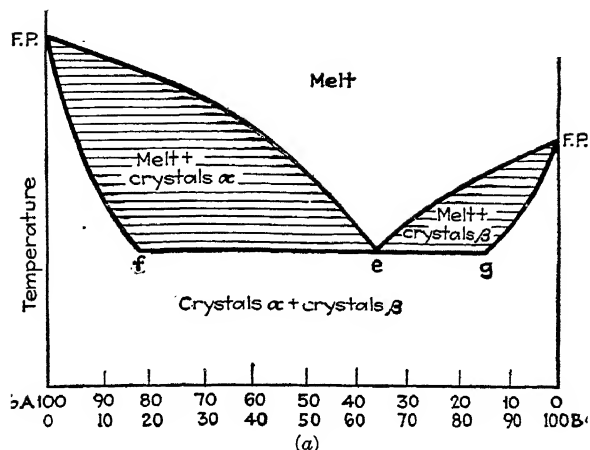
Fig. 126.—(c) Diagram of partial solubility as a composite of three simpler cases shown in (a) and (b) above.

two *liquid* phases as in the ether-water illustration of Fig. 109. This complete diagram is thus composed of three familiar simple types—the eutectic reaction of Fig. 112, parts of the diagram of complete solubility of Fig. 119, and the (now solid) solubility curves *fc* and *gd* of Fig. 109—and is easy to interpret in terms of these three simple cases.

The Structures of Partially Soluble Alloys.—The structure of alloy *x* of this series would be a cored structure on rapid cooling and a one-phase structure upon completion of diffusion; a homo-geneous, one-phase structure just like the completely soluble structures shown in Fig. 121*b*. Alloy *z* would show a similar homogeneous struc-ture (upon complete annealing), ex-cept that since it falls in the two-phase field *fcgd* at room tempera-ture, the homogeneous grains of Fig. 121*b* will have become supersatu-rated with respect to *B* atoms at a temperature below *f* and would pre-cipitate them. The original homoge-neous grains would thus contain a fine

Fig. 127.—Host crystals of alpha-solid solution (dark) with a precipitate of beta crystallites (light) in the grain boundaries and in the crystallographic planes of the host.

precipitate of *d* crystals, appearing as a segregate at the grain boundaries and in the crystallographic planes of the host crystals of·*α*-solid solution as shown in Fig. 127. The separation of this *β* precipitate from the host, in this case *α*-solid-solution crystallites, takes place by a mechanism similar to the formation of a new polymorphic phase in a pure metal. The final com-position of the *α* crystals when they reach room temperature would be that of *c*. The structure is shown in Fig. 127. This structure is called *Widmannstätten.*

Steels show this type of decreasing solubility. For example, the sloping line at the right and left of the lower part of the field marked "*γ*-solid solution" in Fig. 142 shows the decreasing solu-bility of *γ* iron for *α* iron (left) and for carbon (right) as the tem-perature falls. Likewise, the dotted nearly vertical line at the left of the diagram from 700° down to 300°C. shows the decreasing solubility of carbon in *α* iron as the temperature falls.

Alloys z' and y will contain a eutectic matrix of c and d crystals, the z' alloy showing primary α crystallites of composition c; the y alloy primary crystallites of composition d. These crystallites will not be homogeneous but, just like the α crystallites of the z alloy, will also have a fine precipitate of each other at their grain boundaries and within the crystallites themselves, due to the decreasing solubility of A in B as the temperature falls from g to d, etc.

To test your grasp of diagrams for alloys of this type see Problem 3, page 193, for the alloys of copper and silver.

The important age-hardening alloys, such as duralumin, also show this change of solubility with change in temperature as described on page 229. If cooled rapidly from temperature f, as by quenching in water, an alloy such as z in Fig. 126c may be preserved without permitting any precipitate of β to form. On standing, however, the precipitation begins spontaneously and the alloy becomes very hard and strong. Such nonequilibrium conditions are discussed in Chap. VI, page 216.

Rapid Cooling.—Alloy z when cooled in complete equilibrium does not cross the eutectic line, and the last liquid before solidification will not reach the point e; therefore, no eutectic structure would be expected at the grain boundaries. If cooled rapidly, however, as discussed on page 162, the crystalline phase becomes too rich in metal A (owing to lack of diffusion into the cores) and, as a result, the liquid must become greater in amount in B than the diagram shows, since the diagram holds for equilibrium conditions only. With fairly rapid cooling the diffusion (listed at (b) on page 162) is practically zero, and the liquid phase reaches the point e of Fig. 126c. At this point it is saturated in B, and crystals of β-solid solution will separate alternately with α. *A eutectic is obtained in the z alloy.* The same result may be obtained if the x alloy is cooled rapidly. Prolonged annealing, however, will cause all of the eutectic to disappear by diffusion of B atoms into the A-rich cores of primary α grains.

Limiting Cases of Solubility.—It is illuminating to see what would happen to these diagrams if they were distorted to represent extreme cases. For example, suppose in Fig. 126c that points f and g moved out toward the verticals at pure A and pure B, *i.e.*, suppose that a decrease in solid solubility of B in A and of A in B takes place. When f reaches the vertical line

A, and *g* reaches the vertical line *B*, we have duplicated Fig. 112, the simple eutectic. If these two points move inward until they meet, we have a completely soluble alloy series, not exactly like Fig. 118 where the liquidus drops steadily from pure *B* to
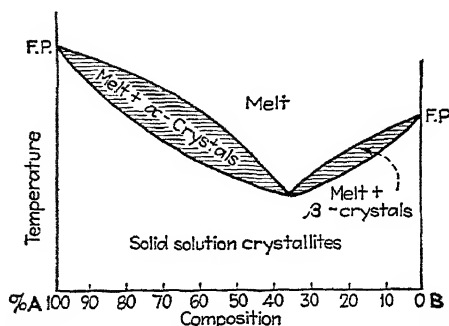
Fig. 128.—Diagram of completely soluble alloys, showing a minimum.

pure *A* but one of the relatively rare ones that show a minimum (see Fig. 128). The only difference between the two is, however, in the particular alloy of composition corresponding to the bottom of the loop. This alloy solidifies as a pure metal would, all
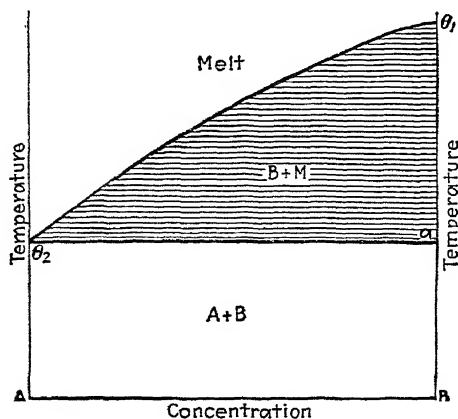
Fig. 129.—Eutectic is pure *A*.

crystals deposited being of the same composition as the liquid. This is one of the particular, rare cases referred to at the beginning of the subject on page 160, in which a completely soluble alloy deposits crystals of the same composition as the melt. It is analogous to a constant-boiling mixture of, say, alcohol and water.

All the other alloys in this series behave as do those in Fig. 118 for copper-nickel. An alloy of this peculiar type occurs in the series iron-chromium, nickel-chromium, nickel-iron, copper-manganese, and copper-gold. For others, see Fig. 256, page 341.

Another limiting case for a simple eutectic would occur if the eutectic point were moved closer and closer to the pure A ordinate. This case would appear as in Fig. 129, in which the eutectic liquid is almost pure A, as described in the beginning of the eutectic discussion. ·

Chemical Compounds and Their Solubilities.—We may now assume that the basic principles of interpretation of binary
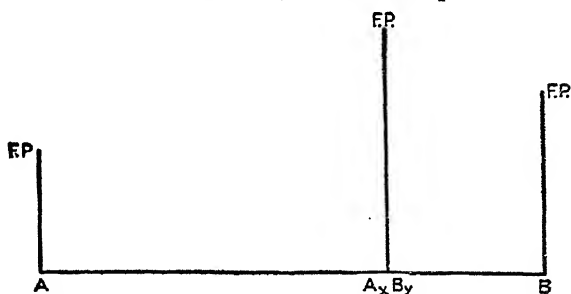
FIG. 130.—Composition and freezing point of pure A, of pure B, and of a compound A_xB_y.

diagrams are understood and that we are ready to advance to the last two cases to be considered. The simpler of these is the case where the combining of two kinds of atoms results not only in liquid or solid *solution* but in a chemical *combination* between the atoms to form a molecule, such as Fe_3C in steel or $CuAl_2$ in duralumin, or, in general terms, a compound, A_xB_y. This combination is shown on the horizontal or composition line of the diagram at the composition of the new molecule A_xB_y, as in Fig. 130. A vertical line should be erected also to show the freezing point or melting point of the compound, assuming that it melts without decomposing and at a constant temperature, as a pure metal or a stable compound, for instance, would do. At once it is apparent that the diagram A-B can be divided into two parts, the one to show all alloys between A and A_xB_y, the other to show those between A_xB_y and B. Actually, it is easiest to consider alloys of this class in this way, and quite correct. When so considered, they are already understood from the types previously studied. For example, the separated diagram for

A-A_xB_y might appear as in Fig. 131*a*, *b*, and *c*.   The compound A_xB_y is shown successively as having complete solubility for A, complete insolubility for A, and partial solubility for A, in the solid state, while the diagrams possible for alloys between A_xB_y and B could appear in similar fashion.   Combining the two parts of the diagram (this time a horizontal combination instead of a
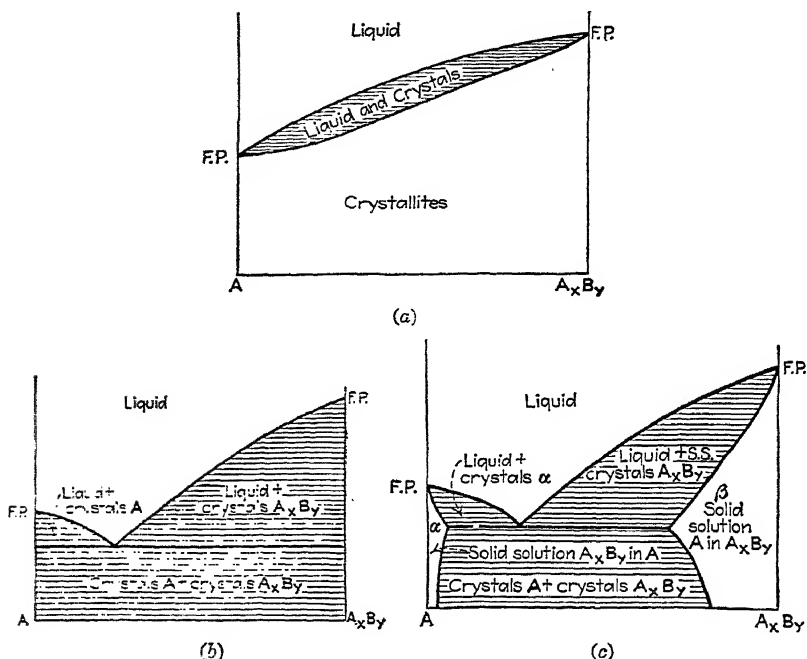
Fig. 131.—(*a*) Complete solubility of pure A and A_xB_y for each other; (*b*) complete insolubility of pure A and A_xB_y for each other; (*c*) partial solubility of pure A and of A_xB_y for each other.

vertical combination as was carried out in Fig. 126), we get complete diagrams such as shown in Figs. 132*a*, *b*, and *c*.   The microstructure of these alloys at room temperature can be predicted very simply; for example, in Fig. 132*a* an alloy *x* would show primary crystals of pure A, surrounded by a eutectic matrix of alternate crystals of pure A and pure A_xB_y.   Alloy *x* in Fig. 132*b* would show primary crystals of A_xB_y surrounded by a eutectic of A_xB_y crystals and B crystals.   Alloy *x* in Fig. 132*c* would show primary β crystals of A_xB_y solid solution of composition *d* (with a segregate in them of α crystallites of com-
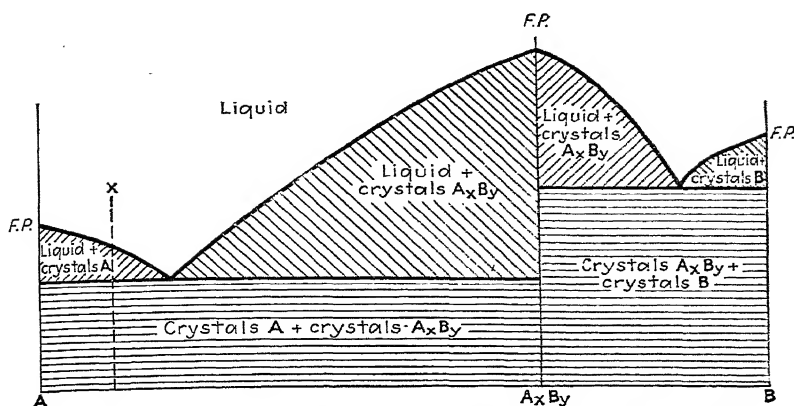
FIG. 132a.—Complete diagram A-A_xB_y-B showing zero solid solubility.
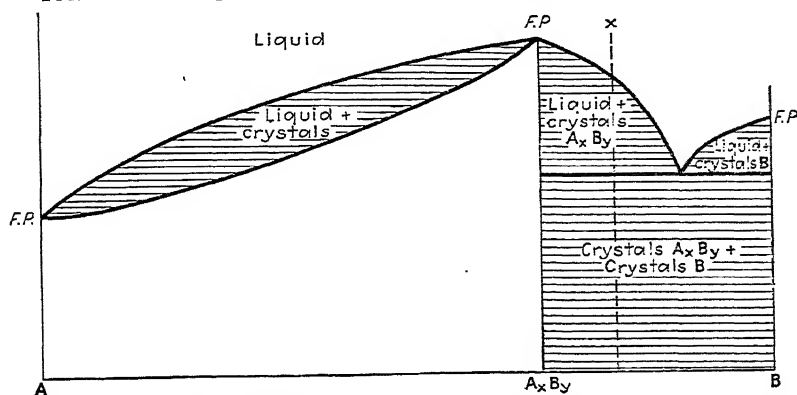
FIG. 132b.—Complete diagram A-A_xB_y-B showing complete solubility of A and A_xB_y for each other; complete insolubility between A_xB_y and B.
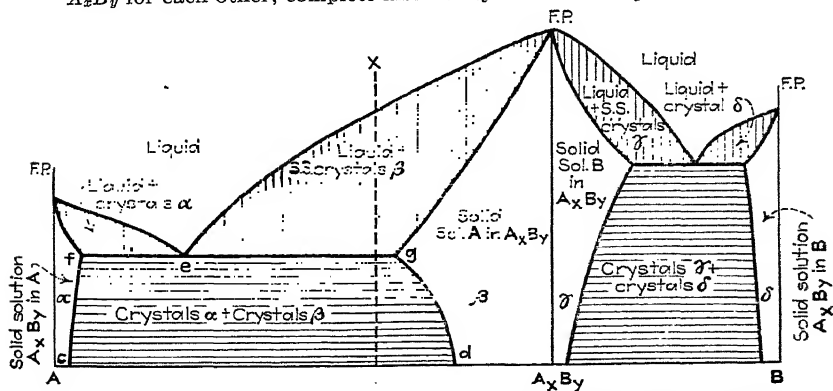
FIG. 132c.—Complete diagram A-A_xB_y-B, showing partial solubility between A and A_xB_y and between A_xB_y and B.

position *c*), set in a eutectic of smaller α and β crystallites. A similar case is that of the microstructure of hypereutectoid steels. This case, in which a chemical compound forms, is thus simple, in that it merely divides the *A-B* diagram into two parts, and that the two diagrams so obtained are combined laterally. In each of the two parts of such a diagram there are only two components present and not more than two. For it is obvious that if the total composition of the alloy lies between A_xB_y and *B*, for
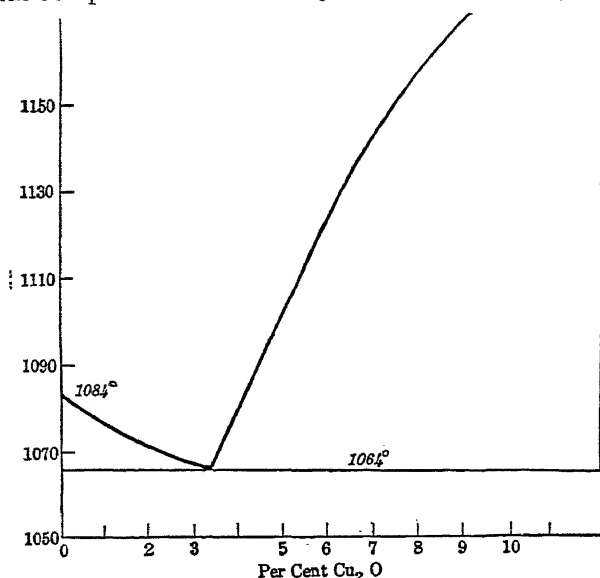
Fig. 133.—Cu-Cu₂O equilibrium diagram up to 10 per cent Cu₂O. (*Courtesy of Homerberg and Williams.*)

example, there cannot be any free *A* material,[1] or it would combine with the excess of *B* to form more A_xB_y. Figure 133 shows an actual diagram, that of Cu and Cu_2O. Figure 134 shows the microstructure of several alloys of Cu and Cu_2O.

To test your grasp of diagrams of this type, try Problem 4, page 193, for the system, magnesium-lead.

The Peritectic Reaction.—The last case to be considered is that not altogether rare one in which a chemical compound or a solid solution cannot withstand heating to its true melting point but suffers decomposition below that temperature. This con-

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[1] Except as the compound A_xB_y may be partly dissociated at any temperature.

dition, it is surprising to note, results again in nothing really new but merely in an *inversion* of the eutectic reaction with which we are already acquainted.

Upon heating an unstable alloy, let us say the compound A_xB_y in Fig. 135, to its decomposition temperature, the A_xB_y crystals
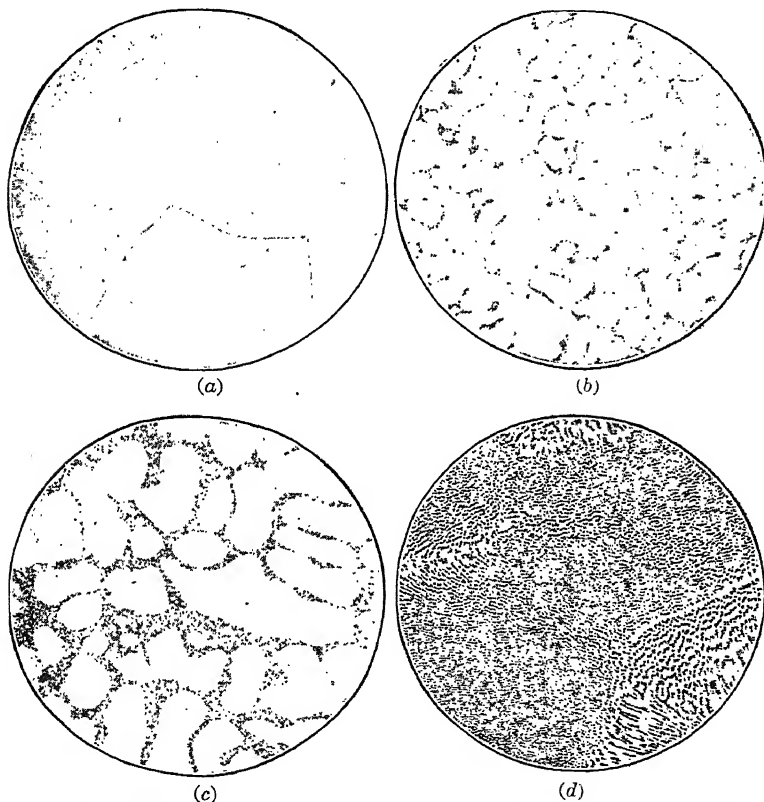
FIG. 134.—Microstructures of Cu-Cu$_2$O alloys: (*a*) pure Cu; (*b*) pure Cu and eutectic; (*c*) Cu + eutectic (higher Cu$_2$O content); (*d*) pure eutectic at 3.3 per cent Cu$_2$O.   (*Courtesy of Homerberg and Williams.*)

would yield a liquid l, which is different in composition from A_xB_y, in this case richer in A.   This liquation leaves crystals that are no longer A_xB_y, but perhaps they are pure B, as shown in Fig. 135.   A homogeneous phase of composition A_xB_y upon *heating* has here decomposed at a certain temperature into two other phases, external in composition to the original A_xB_y, a liquid l and crystals s.   The peritectic reaction is perhaps clearer in

Fig. 136. The separation of liquid l from A_xB_y continues as long as heating continues, until all A_xB_y has disappeared, the temperature remaining constant, owing to the presence of three phases, just as it does in the eutectic reaction. Upon completion of the reaction the alloy now consists of liquid of composition l
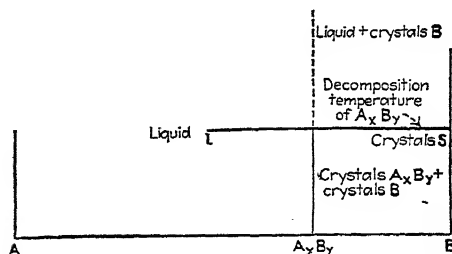
Fig. 135.—Decomposition of a compound below its melting point.

and crystals of composition s in Fig. 135. Further heating causes a rise in temperature and the crystals s gradually dissolve or melt in the liquid, enriching the liquid in B as its temperature rises and causing the liquid to move upward and to the right along the liquidus. The condition is shown in Fig. 136, as is also
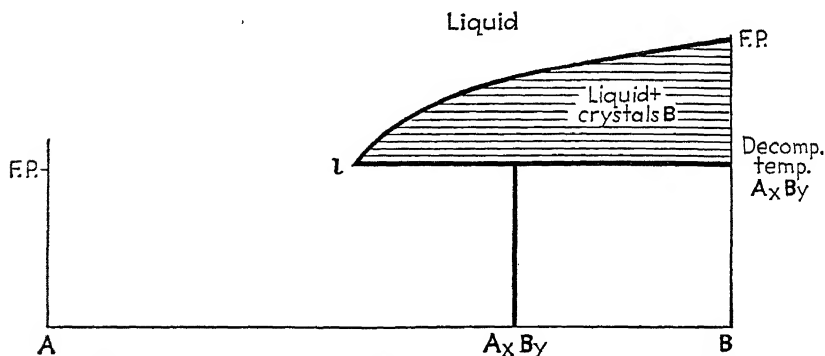
Fig. 136.—Solution of B material in the liquid as the temperature rises following a peritectic reaction.

a complete diagram in Fig. 137. The dotted curve of Fig. 137 shows, at its maximum, the temperature at which A_xB_y would melt if it did *not* decompose on heating. The case is sometimes called the *suppressed*, or *hidden, maximum*.

Upon *cooling* an alloy x in Fig. 137, the reverse process takes place. The original liquid alloy precipitates pure B crystallites (marked s in Figs. 135 and 137) until the reaction line is reached,

the composition of the melt moving downward and to the left along the liquidus toward l. Here the reverse of decomposition, *i.e.*, combination must occur. The liquid, now of composition l, *reacts* with the pure primary s crystals swimming in the melt and forms A_xB_y crystals. The reaction takes place all *around the surface* of each crystal of s where the liquid touches it. Soon a layer of A_xB_y material is formed around every s crystal, and this layer obstructs further access of liquid to the B material inside the
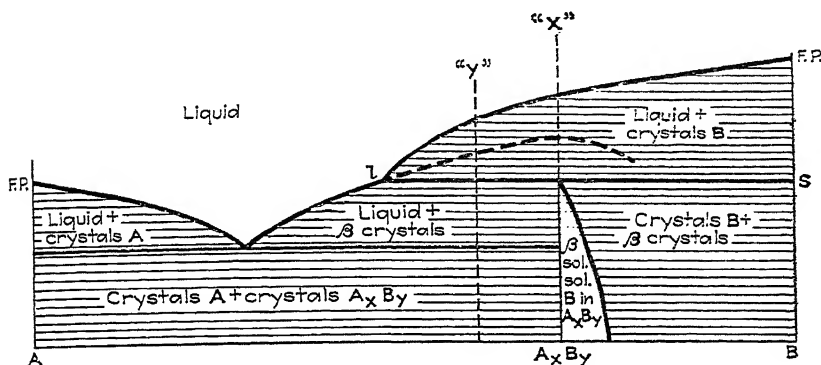
FIG. 137.—Diagram showing A_xB_y formed peritectically at temperature l-s eutectic between A and A_xB_y.

wall or layer. Because of this surrounding wall, the reaction is called a *peri-tectic* reaction—from the Greek *peri* meaning "around." Further reaction is slow since it must wait upon diffusion of more liquid through the peritectic wall of A_xB_y. If diffusion is completed, all liquid will be consumed and also all B material, and nothing left except pure A_xB_y crystallites. The peritectic reaction may be written

$$\text{Liquid } l + \text{crystals } s \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \text{crystals } A_xB_y$$
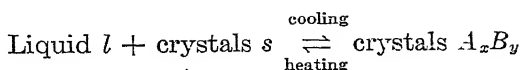
It is recalled that in the eutectic reaction a homogeneous phase (liquid) upon *cooling* decomposes at a certain temperature into two crystalline phases external in composition to the original liquid. The present process is, therefore, just the reverse of the eutectic reaction; *i.e.*, upon heating a homogeneous phase, A_xB_y, it decomposes at a certain temperature into two phases, in this case one liquid and one crystalline. Compare the equations on

pages 155 and 179 to see the similarity.   In the obstructed or nonequilibrium state, the structure of the alloy is shown in Fig. 138, showing the dark-gray peritectic enveloping wall and the unchanged black crystals inside it.

If the total original composition lies not exactly on the line A_xB_y but to the right or left of it, then on cooling there will be left an excess either of liquid (to left of A_xB_y) or of s crystals (to right of A_xB_y) when the reaction is finished.   If the original
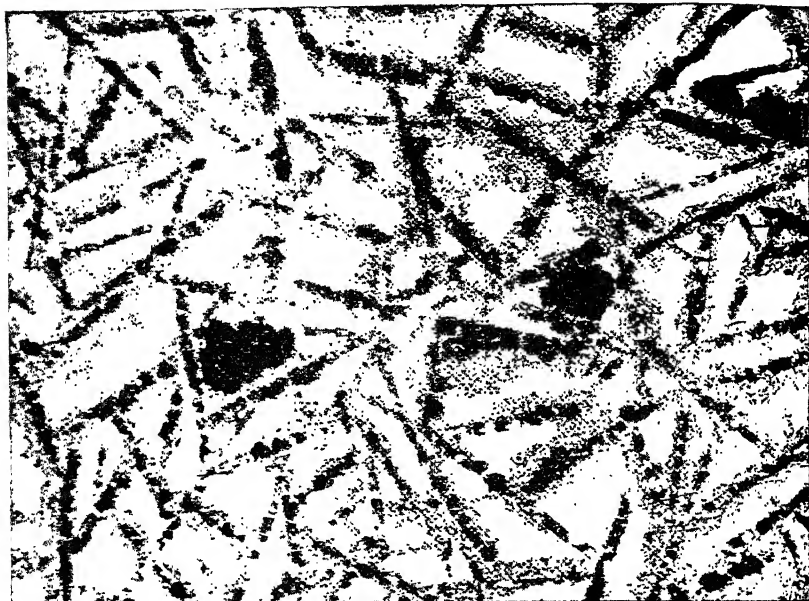
FIG. 138.—Peritectic wall (gray) produced by reaction of melt (now white) with primary crystals (black).   (*Guertler.*)

composition lies between A_xB_y and B, there will be kernels or cores of unchanged B left over when all the liquid is used up and equilibrium is reached, these cores surrounded, of course, by A_xB_y walls.   If the original composition lies between A_xB_y and A, say, at y, there will be an excess of liquid and it will follow down the liquidus from l to the left, depositing pure A_xB_y crystals (at these lower temperatures without necessity of reaction, since it is below the decomposition temperature of A_xB_y).   Finally, the eutectic point is reached in these latter alloys, and the usual alternate deposition of small crystals of A and A_xB_y ensues.   The

final structure of this alloy will be primary crystallites of A_xB_y, formed partly by reaction and partly by simple precipitation, in a eutectic of A_xB_y and A.

This peritectic reaction, the reverse of the eutectic reaction, occurs in many important alloys, such as copper-zinc, iron-nitrogen, and many others. A modification of it occurs when the reaction of liquid and crystals forms a solid solution instead of a chemical compound, as in the δ-γ change of iron-carbon alloys. The results are entirely analogous. An example of a solid solution formed peritectically is shown in the region
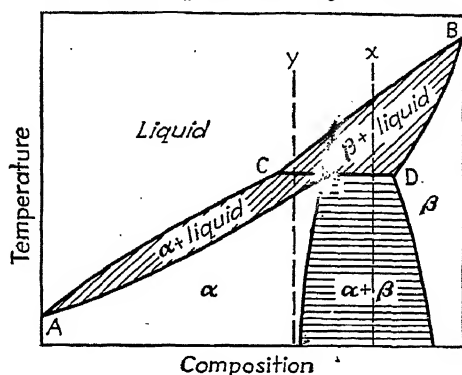
Fig. 139.—Peritectic reaction at CED forming a solid solution (alpha).

marked α in Fig. 139. In cooling the alloy of composition x, Fig. 139, as soon as the temperature reaches the point where it crosses the liquidus, primary solid solution crystals of β begin to precipitate out, the liquid composition following the liquidus down and to the left as the temperature drops until the point C is reached, and the composition of the β crystals following the solidus down and to the left until the point D is reached. At a temperature infinitesimally above the temperature at CD, the percentage of liquid of composition C is $\dfrac{Dx}{CD} \times 100$, and the percentage of crystals of composition D is $\dfrac{Cx}{CD} \times 100$. At the temperature CD, the A-rich liquid at C reacts with the B-rich crystals at D, to form α crystals of composition E. Some D crystals remain without reaction. $\dfrac{Dx}{ED} \times 100$ is now the percentage of α crystals of composition E and $\dfrac{Ex}{ED} \times 100$ is the per-

centage of β crystals of composition D.   In cooling to room temperature, the α crystals precipitate β crystallites and the β crystals precipitate α crystallites.

Alloy y, in cooling, precipitates crystals of β-solid solution upon reaching the liquidus and at a temperature infinitesimally above CD, the percentage of β crystals of composition D is $\dfrac{Cy}{CD} \times 100$

and the percentage of liquid of composition C is $\dfrac{Dy}{CD} \times 100$.

At the temperature CD, the A-rich liquid, C, reacts with the B-rich solid solution, D, to give α-solid solution crystals of composition E but not all of the C liquid is used up in the reaction.
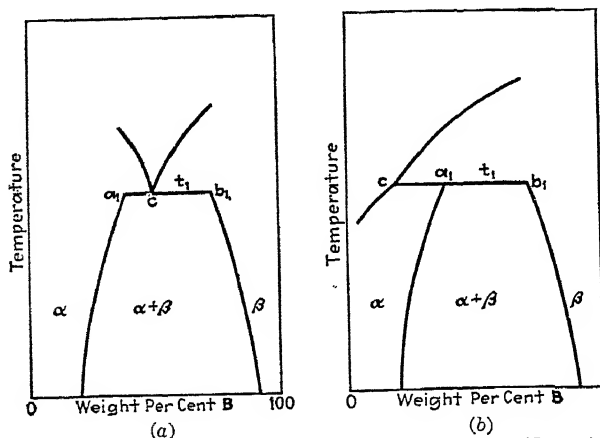
Fɪɢ. 140.—(a) Eutectic reaction; (b) peritectic reaction.   (*Ruer-Mathewson.*)

The percentage of α is $\dfrac{Cy}{CE} \times 100$, and the percentage liquid is

$\dfrac{Ey}{CE} \times 100$.   The liquid C follows down and to the left along the liquidus precipitating α-solid solution until solidification is complete where the vertical line y crosses the α solidus. . Under equilibrium conditions, diffusion is continually taking place from the A-rich liquid and A-rich α-solid solution crystals precipitated below the temperature CD into the relatively B-rich solid solution formed by the peritectic reaction at E.   Upon final solidification, then, we have a homogeneous solid solution, α, which is unchanged in cooling to room temperature.   To test your grasp of this type of diagram, try Problem 5, page 194.

There are other ways of looking at this peritectic reaction to make it clear. For instance, the alloys containing both α and β phases, in Fig. 140b, if heated, form a liquid c, which lies *outside* the limiting composition of either crystalline phase a_1 and b_1, rather than between them as in the case of the eutectic
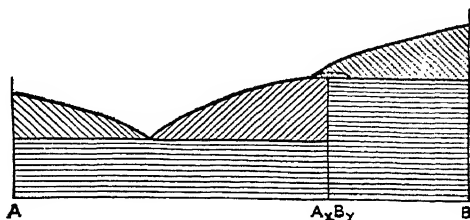
141a.—Compound decomposes below its true melting point (suppressed maximum).
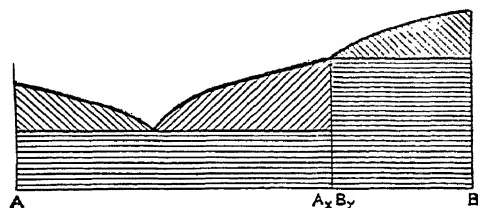
Fig. 141b.—Transition between peritectic and eutectic reaction.
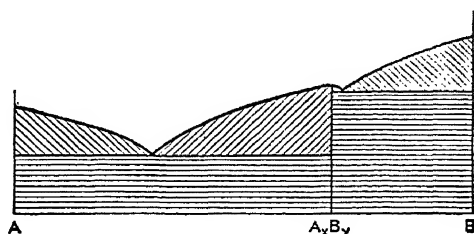
Fig. 141c.—Eutectic reactions.

in Fig. 140a. Or one may say that the liquidus curves of Fig. 140b, intersect, not in a minimum as in 140a, but midway between the freezing points of the pure components, as at c of Fig. 140b.

Limiting Cases of the Peritectic Reaction.—Consideration of the limiting cases of the peritectic reaction will now make clear the conditions under which it occurs. For instance, if the compound A_xB_y did not decompose, it would melt at its "true" melting point as shown by the maximum of the dotted curve of Fig. 137. If the pressure on the system is adjusted, it is sometimes possible

actually to secure melting of an unstable compound without decomposition. The addition of enough of a third element, as in a ternary alloy, also may render the compound stable up to and at its melting point. The transition from a peritectic to a eutectic condition, owing to increased stability of the compound at high temperature, is shown in Figs. 141*a*; *b*, and *c*. The transition in Fig. 139 can be seen by moving point *D* to coincide
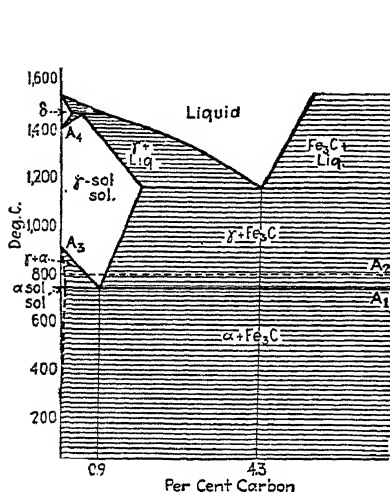
Fig. 142.—Iron-carbon diagram showing eutectoid decomposition of gamma-solid solution.
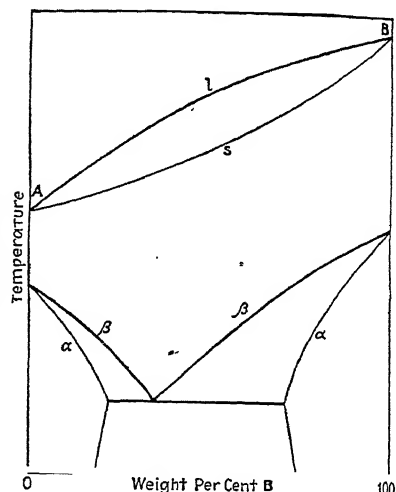
Fig. 143.—Diagram showing complete solubility at high temperatures, partial solubility at lower temperatures. (*Ruer.*)

with *E*. The resulting system is one of complete solubility.[1] The nick at *C* in the liquidus disappears also under these conditions.

Changes in Solidified Alloys.—The very breadth and generality of these types of constitutional diagrams that we have now studied add to their importance. For example, the two components might just as well be two inorganic salts as KCl and NaCl, or NaCl and water, or iron and FeO, or copper and Cu_2O, instead of the two metals, *A* and *B*, which we have chosen as examples.

It is also of the utmost value at this time to point out that these principles hold equally well for changes in the *solid* state of metals and alloys, as well as for the liquid-solid transitions considered up

[1] Like that of copper-nickel in Fig. 118.

to this time. One example of change in the solid state has been given on page 170. We need merely to substitute the words *solid solution* for the words *liquid solution* or *melt* in the diagram for the eutectic and we have, instead of the simple eutectic reaction, the exact case of austenite (solid solution) decomposition in steel to form pearlite, called *eutectoid*, to distinguish it from the liquid reaction, called *eutectic*, which we have studied. In this case, as shown in Fig. 142, the polymorphic transformation point A_3 of γ to α iron, marks the transition from one solid phase to the other instead of the liquid-to-solid change at the melting point in the earlier diagrams, but the case is exactly as simple as the familiar eutectic reaction. Figure 257 is a more complete diagram of the iron-carbon alloys for practical use.

An even simpler example of the use of the diagrams to show changes in the solid state can be given by taking any one of the previously developed diagrams and simply drawing above it another diagram representing the liquid-solid transition. Thus, Fig. 143 shows an alloy series completely soluble at high temperatures but one in which both metals undergo polymorphic transformations at lower temperature and are only partly soluble at low temperatures in the crystalline state.

An Example: Structural Changes in Steel When It Cools Slowly.—Because of its great industrial importance and because it illustrates so many types of structural change, an example in the interpretation of constitutional diagrams will be given for the case of the iron-carbon system. It must be repeated again, however, that no new rules or special instructions, not given in the general cases developed above, are necessary for this or any other binary diagram.

A steel of 0.2 per cent carbon at 1600°C. is a homogeneous liquid as shown in Fig. 142. When its temperature has dropped to about 1520°C. (the liquidus), impure crystals of δ iron (body-centered cubic) containing some carbon in solid solution will precipitate, the melt thus becoming richer in carbon and following down the liquidus and to the right. At the temperature of the horizontal line at 1500° the melt and δ crystals *react* peritectically to form γ-iron solid-solution crystals (face-centered cubic). Since the original composition of the steel lies to the left of the peritectic composition, there will be an excess of δ crystals after the liquid is exhausted. With further drop in temperature
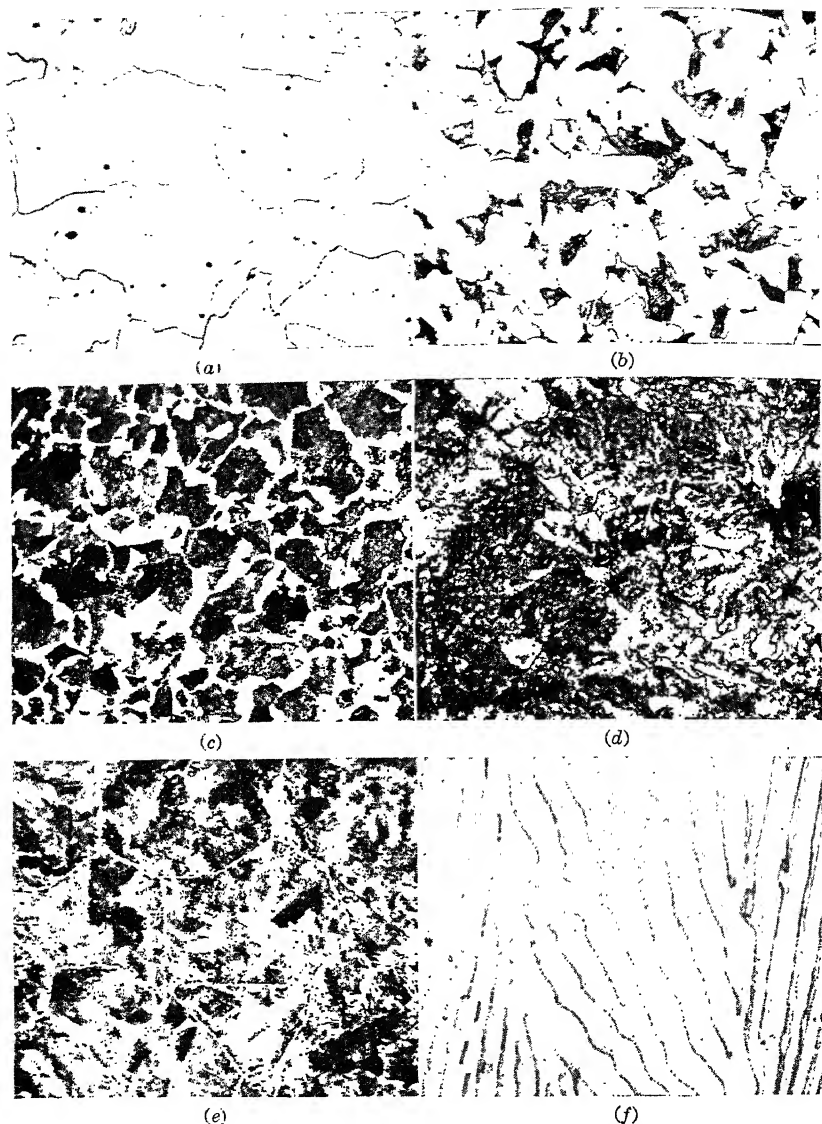
Fig. 144.—Change of microstructure of steel with change in carbon content: (a) Practically carbon-free iron.   ×100.   (b) Steel with 0.25 per cent carbon. Ferrite (white) and pearlite (black).   ×100.   (c) Steel with 0.45 per cent carbon. Ferrite (white) and pearlite (black).   ×100.   (d) Steel with 0.85 per cent carbon. All pearlite.   ×100.   (e) Steel with 1.10 per cent carbon. Pearlite (dark) and cementite (white).   ×100.   (f) Pearlite highly magnified showing lamellar structure.   Ferrite (white) and cementite (black).   ×2,500.   (*Courtesy of United States Steel Corporation Research Laboratories.*)

these δ crystals transform to γ, without interaction of the melt. Slightly above 1400° the structure is entirely γ-iron solid solution (austenite), probably with some coring (see Fig. 122, page 165). From this temperature down to the A_3 line, there is no phase change in the alloy. There may be grain growth or diffusion, or there may be completion of delayed changes, but if equilibrium has existed during cooling there will be no phase change in this field.

When the γ-iron solid solution reaches the temperature of the A_3 line, it has become saturated with respect to α iron and

FIG. 145*a*.—Precipitate of ferrite (white) in a host crystal (originally austenite) black. (*Hanemann.*)
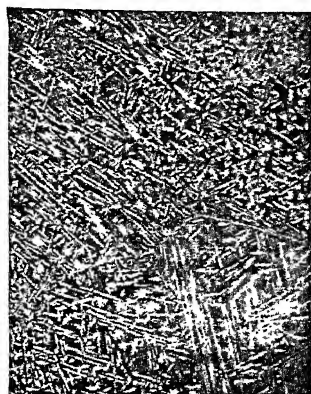
FIG. 145*b*.—Precipitate of alpha constituent in beta host crystallites. (*Hanemann.*)

precipitates α iron at the grain boundaries and in the crystallographic planes of the host γ-solid solution (see Fig. 127). The α crystallites precipitated are *practically* pure iron, since carbon is almost insoluble (actually about 0.03 per cent is soluble at this temperature) in α iron. Removal of iron leaves the austenite grains more concentrated in carbon, and their composition moves downward and to the right with decreasing temperature toward the eutectoid point. Once arrived here, the austenite grains are now saturated likewise in Fe_3C and precipitate alternately α iron (ferrite) and Fe_3C (cementite) until all austenite has disappeared. The alternate precipitate of ferrite and cementite is called *pearlite.* It appears almost solid black in Fig. 144*b* but if magnified to 2,500 diameters the black areas show fine, alternate lamellae of ferrite (white) and cementite (black) (Fig. 144*f*).

This structure remains unchanged down to room temperature, except that the ferrite precipitates a tiny amount of carbon in the form of Fe_3C. In the slowly cooled condition, the structure of iron-carbon alloys and that of α-β brass often appear quite similar, as shown in Figs. 145a and 145b. The precipitating phase has appeared both at the grain boundaries and in the crystallographic planes of the host crystal. This structure is called *Widmannstätten*, for its discoverer. The black background of Fig. 145a is pearlite, unresolved.[1]

Structural Changes in Steel When It Is Heated.—Tracing these changes backward, *i.e.*, during the *heating* of, say, a bar of steel for heat-treatment, or during welding of a steel joint, in order to be sure we understand them, we begin with a structure consisting of ferrite grains in a background of ferrite and cementite lamellae as obtained above on cooling, and as shown in Fig. 144b and f. Until the temperature A_1 is reached, no visible structural changes occur. At this temperature, and before any rise above it can take place, the lamellae of ferrite and cementite in the pearlite begin to dissolve in each other, forming austenite, leaving undissolved the primary (α) ferrite at the grain boundaries and in the crystallographic planes. The early stages in this process are shown in Fig. 146, the arrows pointing to the islands of austenite growing in the pearlite as heating proceeds. In this condition the iron in the ferrite is, of course, magnetic (see Chap. II), while the iron in the austenite has changed to the γ form, having dissolved the Fe_3C lying next to it, and is nonmagnetic. The amount of austenite and of ferrite can, of course, be calculated at this temperature by the use of Rules 1 and 2. During this heating from temperature A_1 upward, the free ferrite at the grain boundaries and in the crystal planes is gradually dissolving in the growing austenite islands, causing the composition of the latter to travel upward and to the left along the A_3 line. When the temperature of the steel crosses this line, all free ferrite has gone into solution and nothing remains except grains of γ-iron solid solution, called *austenite*. If heating is continued to a still higher temperature, these austenite grains grow coarse. Hence in heat-treating to get a fine grain size, steels are usually quenched from a temperature only slightly above that necessary to produce homogeneous austenite (called A_3 *temperature*, see also Fig. 257).

[1] For a complete Fe-Fe₃C diagram see Fig. 257.

Steels that do not coarsen rapidly in the γ range are called *fine-grained* steels (see also page 344). If the quenching is rapid, very little free ferrite has time to collect at the grain boundaries and in the planes; it remains finely dispersed throughout each grain, as explained later under Quenching, page 217. The γ-to-δ change at still higher temperatures is simply the reverse of that described on cooling.

(a)
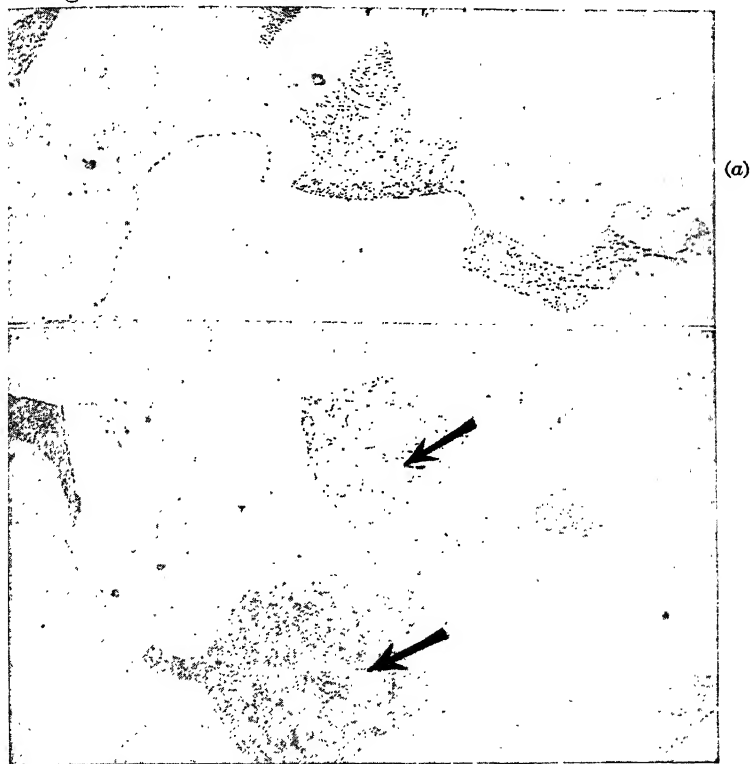
FIG. 146.—(a) A 0.15 per cent carbon steel heated just *below* A_1 and quenched. (b) Same, heated just *above* A_1 and quenched. Arrows show austenite islands (quenched to martensite) forming in pearlite. (*Courtesy of Dr. M. A. Grossmann.*)

The hypereutectoid (above 0.90 per cent C) steels and the cast irons will respond to similar analysis and application of the Rules 1 and 2 given on page 150. Figure 144 shows the microstructure of simple steels of various carbon content.

Review of Binary Equilibrium.—A group of industrially important binary diagrams is shown for rapid review and for selection of alloys according to types of microstructure in Fig. 256. To

illustrate further the vast applicability of these principles, a complex diagram is shown in Fig. 147 so blocked out as to indicate the resolution of each region into a type of diagram which can be readily interpreted, without complications, on the basis of the types previously considered in this chapter.

The equilibrium diagrams for practically all of the binary alloys have been partially investigated.[1] In many of them investigation is, however, still incomplete. In fact, the more
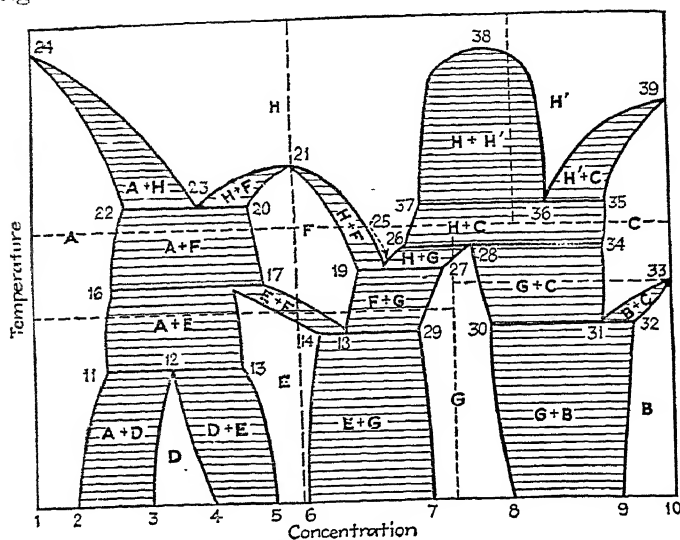
Fig. 147.—Resolution of a complex diagram into simple parts in each dotted block. (*Guertler.*)

exhaustively such a diagram is studied, the more questions of a special nature will arise. This has been especially true of the iron-carbon diagram, which is so very important in industry and which, therefore, has been so very carefully studied. But in other diagrams also there are unanswered questions.

In biological terms, constitutional diagrams of this type may be said to show the genesis or origin of an alloy's anatomy or internal structure and its modification by changes of environment, such as temperature and pressure. It is true that good facility in reading constitutional diagrams is won only by practice in examining a variety of them, just as a mechanical engineer learns to interpret machine designs, or an electrical engineer to

[1] For a discussion of the commercial alloys see pp. 340–373.

read wiring diagrams. Probably this facility is gained more easily by far than is a similar facility in reading "blue prints" or diagrams of mechanical, structural, and electrical designs. To aid the student in obtaining this necessary practice, a number of problems in typical alloy systems are given on pages 192 to 194.

Further Possibilities.—While the breadth of conditions treated in these systems would seem to include all possible cases, we have a great many possibilities left. For instance, if the iron-carbon diagram is carried to higher temperatures, the alloy will boil, and a diagram showing the composition of the vapor phase (of iron and carbon) at various temperatures is shown in Fig. 148. Nor
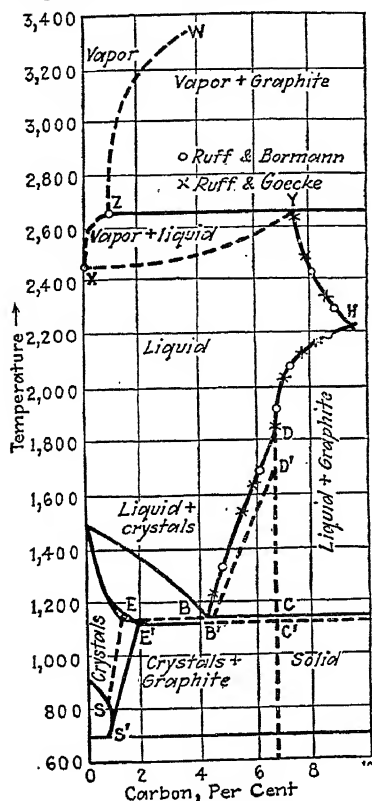
FIG. 148.—System iron-carbon at elevated temperatures.
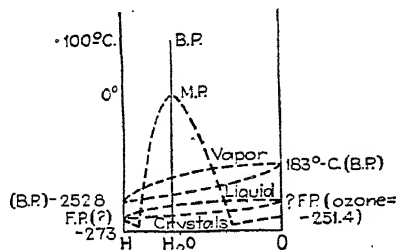
FIG. 149.—Hypothetical diagram of hydrogen and oxygen, showing formation of water in the vapor state.

are these conditions of theoretical importance only. Consider for example the "alloys" of hydrogen and oxygen as in the diagram, Fig. 149. When thoroughly mixed in the liquid state, these two components, hydrogen and oxygen, form no compound. Even above their boiling points these two elements do not combine; and yet, if the temperature be raised several hundred degrees above room temperature, as by an electric spark, a violent combination of hydrogen and oxygen takes place with the formation of a very useful compound H_2O, having a melting

point of 0°C.—*water*. The compound is very stable and has many important uses, and yet it does not form from liquid hydrogen and oxygen. Similar combinations may take place in metallic systems at high temperatures or pressures. The future may show this field to be of great importance. Binary systems composed of oxides such as SiO_2 and MgO interest the geologist. The internal structure of geologic formations of pyromorphic origin thus reveal a part of the history of the earth. In the manufacture of cement, glass, and porcelain, in the study of slags and mattes, these same methods, based on Gibbs's phase rule, prevail.

Problems

1. Aluminum (melting point 660°C.) and silicon (melting point 1420°C.) are assumed to be completely soluble in the liquid state, completely insoluble in the solid state. They form a eutectic at 578°, the eutectic composition being 13 per cent silicon, 87 per cent aluminum.

Required:

1. Draw to scale the constitutional diagram of the alloy system Al-Si, labeling the lines, fields, and points.

2. For the alloy containing 5 per cent silicon, give:

a. The numerical temperature of initial crystallization.

b. When this alloy has cooled to a temperature 15° below *a*, what is the composition of the liquid phase; what proportion is still liquid?

c. Same as (*b*) but with a temperature 15° above *d*.

d. What is the temperature of final solidification?

e. Describe the changes which take place during fall of temperature from initial until final crystallization of this alloy.

f. Plot a time-temperature chart for this alloy on cooling.

3. Same as requirement 2, but for the alloy containing 20 per cent silicon.

4. Same as requirement 2, but for the alloy containing 13 per cent silicon (eutectic alloy).

5. Sketch the general appearance of the microstructure of each of the three alloys if allowed to cool slowly. Label each constituent.

6. Compute the amount of eutectic that would appear in each of the above three alloys at room temperature, assuming that Al and Si have like densities.

2. Gold (melting point 1063°) and platinum (melting point 1760°) are completely soluble in both the solid and liquid states. The solidus and the liquidus show neither a maximum nor a minimum. A 30 per cent platinum alloy begins to crystallize at 1400° by separating crystals of 70 per cent platinum.

Required:

1. Draw the constitutional diagram to scale.

2. For an alloy containing 20 per cent gold, assuming complete equilibrium, give:

a-1. The numerical temperature of initial, and

a-2. Of final crystallization.

b. At a temperature 30° *below a*-1, give the composition and relative amount of the liquid phase present; also composition of the solid.

c. Same at a temperature 50° *above a*-2.

d. Plot a time-temperature chart of this alloy during cooling.

3. Same as requirement 2, but for alloy of 80 per cent gold.

4. Describe the crystallization of the 20 per cent gold alloy as it passes points specified in requirements 2*a*-1, 2*b*, 2*c*, and 2*a*-2, complete equilibrium being assumed.

5. Sketch the general appearance of the microstructure of each of the two alloys if cooled *rather rapidly*.

3. Copper melts at 1083°C., silver at 961°C. A eutectic is found at 72 per cent silver, the temperature being 778°. The solid solubility of silver in copper at this temperature is 7 per cent; of copper in silver, 9 per cent. Assume that the solubility of each at room temperature is 1 per cent.

Required:

1. Draw to scale the constitutional diagram, labeling the fields.

2. Describe the crystallization of a 20 per cent silver alloy and sketch its microstructure giving composition of each constituent at room temperature. What proportion of eutectic will it contain? Plot the time-temperature chart of this alloy.

3. Same for the eutectic alloy.

4. Same for 96 per cent silver alloy.

5. According to this diagram, would sterling silver (92.5 per cent silver, rest copper) be a homogeneous alloy? Would it show any eutectic if rapidly cooled? Why or why not?

4. Magnesium (650°) and lead (327°) form a compound Mg_2Pb which melts at 550°. This compound forms a eutectic with pure magnesium. The eutectic composition is at concentration 67 per cent lead; the eutectic temperature is 455°. A second eutectic is formed between the compound Mg_2Pb and pure lead. It is at concentration 97 per cent lead; assume its melting temperature is 275°. The compounds are completely soluble in the liquid state; completely insoluble in the solid state.

Required:

1. Draw to scale the constitutional diagram labeling the fields.

2. Describe the cooling and crystallization of a 50-50 alloy and sketch its microstructure when it has cooled to room temperature. What proportion of eutectic will it contain? Plot the time-temperature chart of this alloy during cooling.

3. Same as requirement 2, for an alloy of 75 per cent lead.

4. Same as requirement 2, for an alloy of 90 per cent lead.

5. Sketch the microstructure of each of the three alloys noted, and label each constituent.

5. *Required:*

1. Choose a binary system in which one or more peritectic reactions occur. Describe this system so it could be plotted from description.

2. Plot the constitutional diagram of the chosen system.

3. Describe minutely and completely the cooling of a peritectic alloy and sketch microstructure; (a) with complete diffusion; (b) with only slight diffusion.

4. Plot the time-temperature chart of this alloy under the above conditions of cooling.   (See part 3a and b.)

5. Sketch the diagram of an important industrial alloy series which shows a peritectic reaction.   Sketch the microstructure of one alloy of this system, assuming rapid cooling.

6. Plot the systems Al-Cu, Cu-Zn, and Fe-C.   Mark each one off into blocks as in Fig. 147, page 190, each block containing only one reaction.

7. Two specimens of steel, *A* and *B*, may be regarded as composed either of ferrite (Fe) and cementite (Fe_3C), or else of Fe_3C and pearlite, or ferrite and pearlite, depending on the carbon content.

A is sheet steel containing 0.20 per cent C.   *B* is spring steel containing 0.95 per cent C.   The specific gravity of ferrite is 7.86; of Fe_3C, 7.66.

Required:

1. When *A* and *B* are cooled from the molten state, at what temperatures do they begin to crystallize, and at what temperatures is solidification complete?

2. What will be their metallographic compositions just after freezing and at room temperature, regarded in each of the above ways?

3. If sections of *A* and *B* are examined under the microscope, what percentages of the field will be occupied by ferrite and by Fe_3C?

4. Above what temperatures should *A* and *B* be heated before quenching to obtain the maximum hardening effect?

5. A steel is composed of 40 per cent pearlite and 60 per cent ferrite. How much carbon does it contain?   How much Fe_3C?

6. A photomicrograph of steel shows 10 per cent of the area occupied by Fe_3C, and 90 per cent by ferrite.   How much carbon does the steel contain? How much pearlite?   From A. Butts, "A Textbook of Metallurgy Problems."

GIBBS'S PHASE RULE[1]

Nomenclature.—As was stated at the beginning of this chapter, the phase rule of J. Willard Gibbs is the foundation of the entire study of heterogeneous equilibrium with which we have been

[1] See also Rivett, A. C. D., "The Phase Rule." Oxford University Press, New York; 1923.

dealing. A brief examination of this important scientific generalization is essential to the treatment of the subject. It was not given earlier in the chapter because it was felt wiser to stress the *uses* of constitutional diagrams rather than their *derivation*.

Gibbs's phase rule predicts the number of phases P that may be present in a system of C components under a given set of conditions of temperature, pressure, and volume. Thus, for example, a binary $(C = 2)$ alloy may in a particular case exhibit three $(P = 3)$ kinds of crystals even when annealed for a long time $(temp. = \text{variable})$. The doubt whether a longer annealing can avail in removing one of the kinds of crystals by diffusion can be answered by the application of the phase rule to the system, as we shall see below. The practical importance of the rule is thus illustrated in the annealing operation.

The Term "Phase."—In the terms of Willard Gibbs,[1] a phase is a portion of matter, homogeneous in the sense that its smallest mechanically isolable parts are indistinguishable from one another. We may call such bodies as differ in composition or state, different *phases* of the matter considered, regarding all bodies that differ only in quantity and form as different examples of the same phase. Homogeneity in the sense intended is a term applicable to a mixture of gases or to a solution of one substance in another. Thus, there can be only one vapor phase (all gases being completely miscible) but several liquid and crystalline phases.

The Term "Variable."—Since a particular phase may be able to exist under various conditions of temperature, pressure, and specific volume (or concentration), it is usual and convenient to refer to these factors as the variables of the phase.

The Term "Component."—To indicate the minimum number of molecular species in terms of which the compositions of all phases in that system may be quantitatively expressed (Nernst) the term *component* is used. Thus, in the system copper-aluminum, which contains the compounds CuAl and CuAl$_2$, all compositions may be expressed by the molecular species Cu and Al. Therefore, it is a two-component system.

Derivation (Nonmathematical).—Suppose that P phases exist in equilibrium with one another, and that their compositions

[1] "Scientific Papers of J. Willard Gibbs," *Trans. Connecticut Academy,* 1874–1878.

may all be expressed in terms of C components.   For each phase there will be an equation connecting its variables: pressure, temperature, and volume (or its reciprocal, concentration); for example, $f(p, t, v) = 0$.   For a system of P phases there will be P single-phase equations of this type.   Also the P phases may be arranged in $P - 1$ pairs,[1] so that there will be $P - 1$ phase-equilibrium equations for each component or in all $C(P - 1)$. The total number of equations is, thus, $P + C(P - 1)$.

The variables will be pressure, temperature, and the concentration of each component in each phase; altogether $C \times P$ concentrations.   The total number of variables is thus $2 + CP$ (the figure is 2 instead of 3 because, if pressure and temperature be fixed, then the volume is fixed also).

The number of variables *minus* the number of equations connecting the variables must be the number of quantities that must be fixed to define fully the system or the number of degrees of freedom of the system, represented by F.   Thus, if the number of equations is equal to the number of variables, the system will have no degree of freedom but will be completely specified.   In general terms

$$F = (2 + CP) \text{ minus } [P + C(P - 1)] = 2 - P + C.$$

This simple relation, first worked out from thermodynamic considerations by Prof. J. Willard Gibbs at Yale University, is called the "phase rule."

Examples.—For a one-component system, the equilibrium conditions have been shown on page 13.   For a two-component system, such as the simple eutectic diagram of Fig. 112, page 155, we may apply the phase rule as follows:

I. In the region above the liquidus we have
   Number of components (A and B) = 2
   Number of phases[2] (liquid) = 1
   Applying the rule, $F = C + 2 - P$
   $\qquad\qquad\quad = 2 + 2 - 1$
   $\qquad\qquad\quad = 3$ degrees of freedom

---

[1] In a three-phase system, if phases I and II are in equilibrium, and phases I and III are, then II and III *must* be so, hence $P - 1$ equations—for each component, or $C(P - 1)$ altogether.

[2] No vapor is present in these examples, although under atmospheric conditions the vapor phase is always present.   The nitrogen, oxygen, and argon

That is to say, we may change the temperature, the concentration, and the pressure of the liquid phase without destroying the equilibrium, *i.e.*, without introducing a new phase or exterminating one. If we choose to work at atmospheric pressure, as has been done in the investigation of almost all the binary systems published, then one of the degrees of freedom has been exercised and but two are left.

II. In the field between the liquidus and the solidus we have
   Number of components (A and B) = 2
   Number of phases (liquid, crystals A or B) = 2
   $F = 2 + 2 - 2$
     = 2 degrees of freedom

In this region two degrees of freedom exist. If the pressure is fixed at one atmosphere, then but one degree of freedom is left and any change in temperature will cause a corresponding change in the concentration of *each* phase, as shown by the slopes of the liquidus and solidus curves.

III. At the eutectic temperature e we have
   Number of components (A and B) = 2
   Number of phases (liquid, crystals A *and* crystals B)
     = 3
   $F = 2 + 2 - 3$
     = 1 degree of freedom

In case III, if the pressure is fixed at one atmosphere, then the one degree of freedom has been exercised and a change of either temperature or concentration will cause a phase to disappear. If the temperature is lowered, the liquid disappears. If it is raised, either A or B crystals or both disappear.

   Thus, in a two-component system during the solidification of a eutectic or peritectic alloy at a fixed pressure, the temperature of the system *and* the composition of the three phases *must* remain constant, as indicated by the straight horizontal line drawn at that point in the diagram and shown by the cooling curve of the alloy.

of the atmosphere become components of the system being investigated and raise it, in this case to a *five*-component, instead of a *two*-component, system. The number of degrees of freedom is, of course, correspondingly increased.

Clearly, if any binary alloy shows three solid phases after a homogenizing heat-treatment, *i.e.*, when the temperature is varied, it indicates merely that the treatment has not been complete. An unintentional third component, such as an undetected impurity, must, of course, be guarded against in these conclusions, as such an impurity really supplies an additional component to the system.

It thus becomes apparent that the equilibrium diagrams in this chapter are all expressions of the phase rule. This derivation of the diagrams has not been stressed previously because such derivation often becomes a substitute for practice in the use of these diagrams in handling metallic problems; for the metallurgist, it is in the use of these diagrams, to test their procedures and plan their programs, that their greatest value lies, not in a study of the principles that they illustrate.

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CHAPTER V

THE CRYSTAL STRUCTURE OF BINARY ALLOYS

Now that the microstructures of binary alloys and the modes of origin of these structures are understood, it becomes of interest to go deeper and to inquire also into the atomic arrangements within each of the individual grains of which the structure is composed. For, although the microscope tells us when a new phase has appeared, or when solubility has been exceeded, it tells
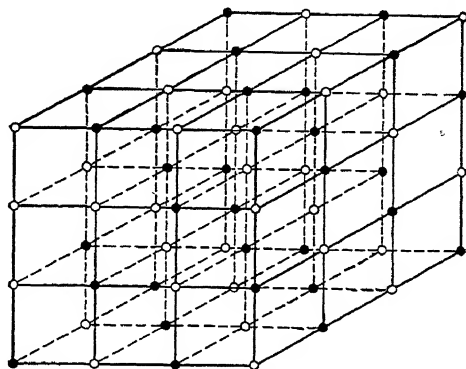
Fig. 150.—Diagrammatic illustration of a substitutional solid solution.

us nothing about changes that may occur in the crystals when a new phase does *not* appear, *i.e.*, for example, when the two components form a solid solution of variable composition. In Chap. I the crystal structure of pure metals (pure *A* or *B*) has been examined. It seemed best to study also equilibrium in solid solutions, as is done in Chap. IV, before taking up the crystal structure of alloys as will be done now.

Substitutional Solid Solutions.—In the crystals of a pure metal each point in the space lattice is occupied by the same kind of atom. In the most common type of solid solution some of these atoms are replaced by "dissolved" or foreign atoms. This type of solid solution is called a substitutional solid solution, and is illustrated in Fig. 150. The solid dots indicate the position

of the host atoms A and the open circles indicate the substitution of the foreign atoms B in the case of a 50 atomic per cent solid solution.[1]   The great majority of the solid solutions are of this substitutional type.   The distribution of the foreign atoms is not necessarily uniform in every cell, but is statistically so over the entire crystal.   Because the atomic volume varies from element to element, it immediately becomes evident that the substitution
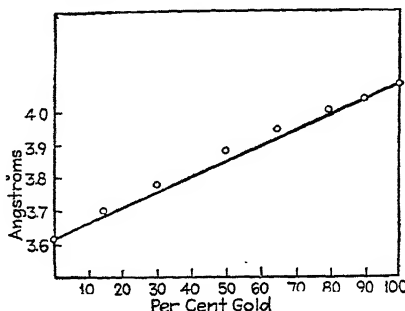
Fig. 151.—Change of lattice parameter of (quenched) gold-copper alloys with change of composition.

of foreign atoms for native atoms in the host lattice must necessarily involve a change in parameter of that lattice.   If the solute atom is larger than the solvent atom, the change will be an expansion of the solvent lattice; if it is smaller, the change will be a contraction.   Vegard's law, which was first derived for solid solutions in ionic crystals and which has since been extended to metallic solid solutions, states that the lattice parameter of the solid solution varies linearly with the percentage of solute present. In some cases this law holds within the limits of experimental error, but in most cases it must be regarded only as a first approximation, as other factors besides atomic volume enter in.   The change in lattice parameter for quenched Cu-Au alloys is shown

[1] Atomic per cent instead of weight per cent requires that the *number* of atoms shown on the horizontal scale be 100, instead of the total *weight* of the atoms being 100, as in previous diagrams.   If the weight of each of the two kinds of atoms is known, it is simple to calculate the relative number of atoms.   If an alloy is composed of p per cent of the element A, of atomic weight A, and of q per cent of the element B, of atomic weight B, then its

A content in atomic per cent is $\dfrac{100\,p}{p + q\left(\dfrac{A}{B}\right)}$ and its B content is $\dfrac{100\,q\left(\dfrac{A}{B}\right)}{p + q\left(\dfrac{A}{B}\right)}$.

in Fig. 151. Complete miscibility of two metals in the solid state is possible only when the crystal structure of each metal is of the same type, *e.g.*, when both are body-centered cubic. The actual
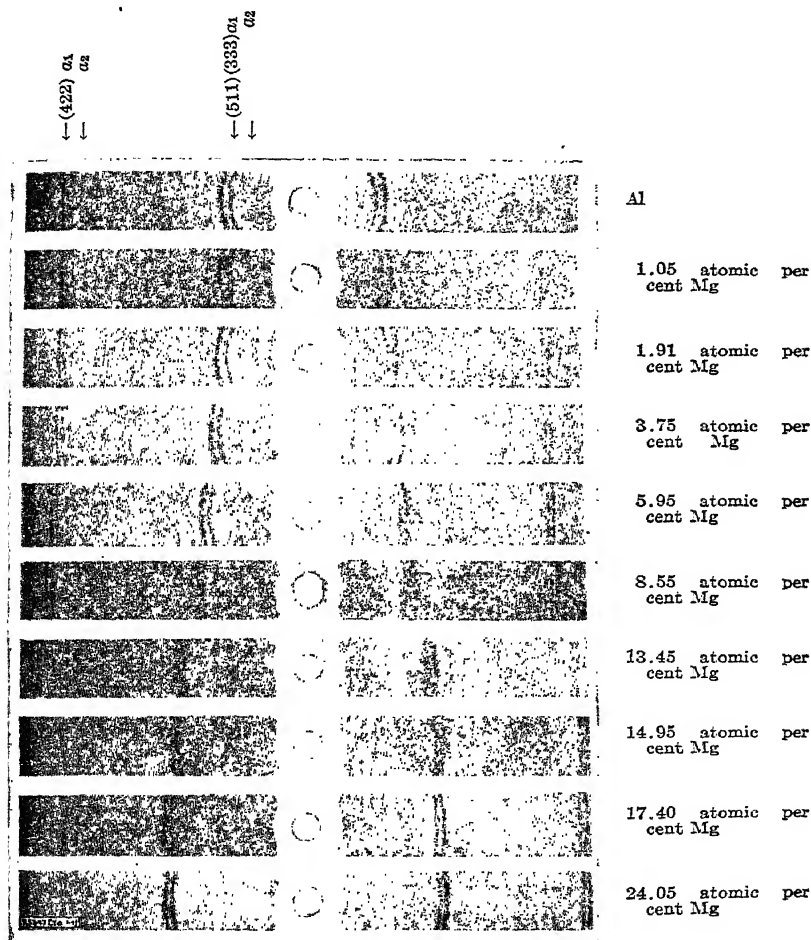
Fɪɢ. 152.—Expansion of aluminum lattice with increasing magnesium content.
(*Schmid and Siebel.*)

spectrograms for the series Al-Mg are shown in Fig. 152. These spectrograms show by progressive increase in diameter of the black rings the expansion of the Al lattice as the concentration of the Mg increases up to 17 atomic per cent Mg. Above 17 per

cent Mg no change takes place, because the Al crystals are saturated with Mg atoms.

Sometimes a series of binary alloys which appear to be completely soluble under the microscope do, nevertheless, when examined by X-ray diffraction, show changes in the lattice form, rather than a simple expansion of the host lattice. Thus McKeehan[1] finds the nickel-iron alloys from 0 to 25 per cent nickel have chiefly a body-centered cubic lattice, of parameter 2.86 to 2.89 Å. From 0 to 70 per cent iron the alloys have the face-centered cubic lattice of nickel, with parameter 3.499 to 3.600 Å. In the intermediate region either or both lattices may exist. These differences are not distinguishable by the aid of the microscope, and the alloys appear as a continuous series of solid solutions. In a special case more recently examined, that of the copper-manganese alloys, there is a gradual transition from the cubic face-centered copper lattice to the tetragonal lattice of manganese. This extraordinary transition from one phase (cubic) to another phase (tetragonal) is of theoretical interest in connection with Gibbs's phase rule.

Theoretical Considerations.—In view of the foregoing discussion of the substitutional solid solution, it will be of interest to examine some of the factors limiting solid solubility. Hume-Rothery[2] and his coworkers have probably contributed most to the theories and correlation of data in this field and it is upon his work that the following discussion is based.

Since the formation of a solid solution involves a change in dimensions of the solvent or host lattice, it is only natural to expect that there should be a relationship between the atomic diameter of the solute atoms and the limit of the solubility of those atoms in the host crystal. As a result of a survey of the alloys of Cu and Ag with the elements of the *B* subgroups (see periodic chart), Hume-Rothery, Mabbot, and Channel-Evans have postulated the following theory. Other things being equal, a difference in atomic diameter of less than 14–15 per cent of the solute and solvent atoms results in extensive solid solution, while if the difference is greater than 14–15 per cent, the size factor is unfavorable and solid solubility is limited. Whether or not such limits

[1] *Phys. Rev.*, **21**, 402, 1923.

[2] Hume-Rothery, W.: "The Structure of Metals and Alloys," Institute of Metals, London, 1936

are valid for all solid-solution systems remains to be seen. Investigation to date indicates that the same size factor holds for Mg and Fe alloys.

If the size factors are favorable according to the above concept, another factor limiting solid solution is the tendency for the two metals to form a stable intermediate compound. These resemble the normal valency compounds, such as NaCl. It may be stated that, in general, the more electropositive the solvent and the more electronegative the solute, the greater is the tendency to form stable intermediate compounds. Thus in the Mg-S system, the compound corresponding to MgS is formed at 50 atomic per cent. Mg has a valence of $+2$, while S may be thought of as having a valence of -6. MgS would then correspond to the ionic type valence compound. This tendency to form stable intermediate constituents is termed the *electronegative valency effect*. The formation of such constituents tends to limit markedly the solid solubility, even if the above-mentioned size factor is favorable.

The extent of solubility of Mg in Au is different from that of Au in Mg. This is generally true—that the reciprocal solubilities in a binary system are not equal. It has been found that the more electropositive metal is capable of dissolving more of the electronegative metal than vice versa. This effect is known as the *relative valency effect*. Thus, in the Cu-Zn system, when the size factor is favorable, Cu can dissolve 38.7 per cent of Zn, while Zn dissolves only 2.3 per cent Cu. It can be shown by means of quantum mechanics and Pauli's principle that the number of valence electrons that can be added to a given lattice is limited. With this in mind, we should expect that a given lattice would dissolve one-half as much of a divalent element as of a univalent element, and one-third as much of a trivalent element as of a univalent element, provided the size factors were favorable in each case and the tendency to form intermediate compounds were not too great. This has been generally found to be true—*e.g.*, the trivalent elements Al, In, and Ga have solubilities of the order of 20–21 per cent in the systems Cu-Al, Cu-Ga, Ag-Al, and Ag-In, while the divalent elements Zn and Cd have maximum solubilities of the order of 40 atomic per cent.

Superlattices.—The distribution of the foreign atoms in the host lattice is usually random. In rare cases, however, solid

solutions that have a random distribution of atoms at high temperatures undergo an atomic rearrangement at lower temperatures, and the foreign atoms take up definite and periodic positions on the host lattice. Such definite positions give rise to their own sets of X-ray interference lines. This periodic structure, or
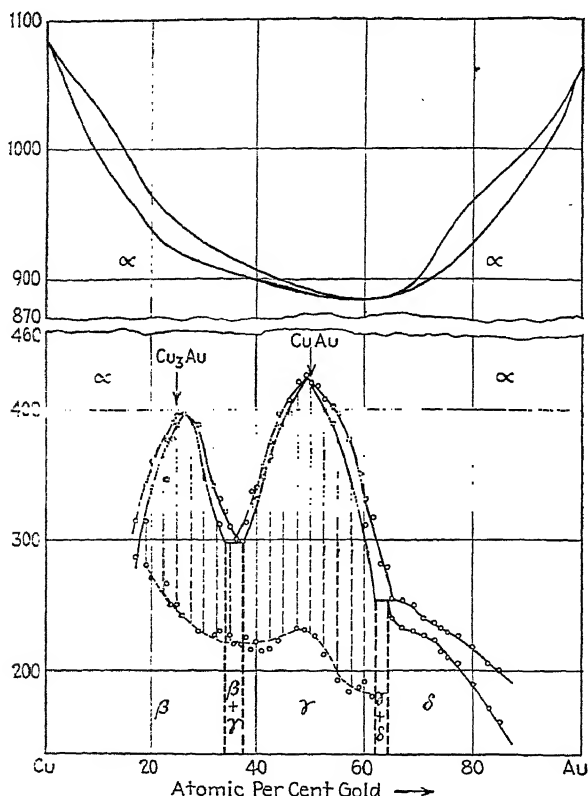
Fig. 153.- -The system copper-gold showing compounds below 460°C. which exhibit superlattices.

superlattice, was named by the Germans *Überstruktur*. It is found that in many cases these structures occur at definite concentrations corresponding to multiple proportions of the two kinds of atoms. Of particular interest are the alloys of Cu_3Au and $CuAu$ in the system Cu-Au shown in Fig. 153. At elevated temperatures they are solid solutions (random distribution of atoms) and at lower temperatures show a uniform distribution of

foreign and native atoms corresponding to the definite intermediate phases Cu_3Au and $CuAu$. At 25 atomic per cent Au, corresponding to Cu_3Au, the Au atoms occupy the corners of the cube while the Cu atoms occupy the centers of the faces, as shown in Fig. 154. The equiatomic alloy, CuAu, presents a structure as shown in Fig. 155. The intensity of reflection from an atom, *i.e.*, its efficiency as a scatterer of X rays, is proportional to its atomic number, making it possible to identify the location of heavier atoms in the case of a superlattice by this means. The formation of a superlattice is often accompanied by definite changes in mechanical and electrical properties of the alloy.
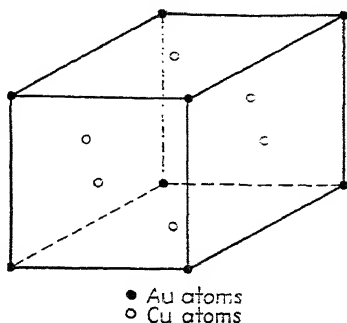
● Au atoms
○ Cu atoms

FIG. 154.—Diagrammatic illustration of 25 atomic per cent Au alloy in the Cu-Au system.

The electrical conductivity frequently rises to a maximum. Rather than regard these superlattices as definite compounds, it is more correct merely to regard them as involving an atomic rearrangement that enables the atoms to fit together with a lower energy content and hence a greater stability. The β-β' solid solutions in the brasses, Fig. 269, Chap. XII, are another example of the same kind. The β' solution shows a superlattice; β does not.

● Au atoms
○ Cu atoms.

155.—Equiatomic alloy in the Cu-Au system,

Intermediate Constituents (Intermetallic Compounds).—In many metallic systems additional constituents are formed whose compositions are intermediate between the two primary solid solutions. These intermediate constituents usually correspond to certain definite compositions and may be conveniently designated by means of chemical formulas, *e.g.*, Cu_3Al, $CuZn$, Mg_2Sn. These intermediate phases often exhibit properties entirely different from those of either of the constituent metals, and frequently crystallize in complex crystallographic systems. Their corresponding lower order of crystal symmetry

and fewer planes of dense atomic population may be associated with these differences in properties, *e.g.*, greater hardness and lower electrical conductivity. These intermediate constituents frequently enter into rather extensive solid solution with their component elements, the lattice of the compound serving as host, for the dissolved atoms. The great variety of properties obtainable in modern industrial alloys is largely dependent upon these intermediate constituents and their solid solutions. Table VIII shows the crystal structure of some intermetallic compounds.

TABLE VIII.—CRYSTAL STRUCTURE OF INTERMETALLIC COMPOUNDS[1]

Compound	Lattice type	Compound	Lattice type
Cu_2Zn_3	Cubic	$CuZn_2$	Trigonal
Al_3Mg_4	Cubic	$CuAl_2$	Tetragonal
$NaCd_2$	Cubic	$FeSi_2$	Tetragonal
$FeSi$	Cubic	$NiAs$	Hexagonal
Mg_2Sn	Cubic (CaF_2 type)	$NiSb$	Hexagonal
Mg_2Si	Cubic (CaF_2 type)	$CuAl$	Rhombohedral
$MgPb_2$	Cubic (CaF_2 type)	Fe_3C	Orthorhombic

[1] CLARK, GEORGE L., "Applied X-rays," 2d ed., p. 202, McGraw-Hill Book Company, Inc., New York, 1932.

Interstitial Solid Solutions.—In addition to the substitutional solid solution, a second type is encountered when the solute

FIG. 156.—Diagrammatic illustration of an interstitial solid solution. Interstitial elements may be located at *x* relative to the parent lattice *i*.

atoms are of a very much smaller diameter than the solvent atoms. Here the solute atoms fit into the spaces between the solvent atoms in the lattice and form the same general types of solutions and compounds as are formed in substitutional solid solutions. The same factors of size, normal valency, and relative valency are important in this case. Naturally this "interstitial" type of solid solution leads to higher densities than does the substitutional arrangement of atoms. The elements chiefly concerned are H_2, N_2, C, and B, and many of their compounds are of particular interest, especially those formed with iron, such as Fe_3C and Fe_4N. This type of solid solution forms

the basis for steels.   Figure 156 illustrates how these small atoms may be substituted interstitially.   The host lattice in this illustration is a face-centered cubic structure, and it is desired to fit small atoms into the lattice.   They can occupy either the positions marked x, between the atoms, or the positions i, in the centers of the small cubes.

It may be stated, as will be pointed out later, that diffusion of the solute atoms through the lattice in this type of solid solution is usually more rapid than in the substitutional type, owing probably to their small atomic size and relative freedom of passage.

The Diffraction Patterns of Duplex Alloys.—The diffraction pattern of a duplex alloy or aggregate, as for instance that of a eutectic, shows the pattern due to each kind of crystallite separately.   Thus the X-ray method may be used to determine the boundaries of the one- and two-phase fields in a whole series of binary alloys.

The Determination of Solubility Limits by X Rays.—In certain instances either the X-ray or the microscopic method can be used in the investigation of alloy constitution.   In other instances only one or the other is applicable.   The lattice structure of solid solutions requires, of course, X-ray analysis, atomic structure being far too fine for visibility, even with the most powerful microscope.   The extent of solid solubility, on the contrary, may be investigated by either method.   An example of this use of the X-ray methods may be of interest.

For the solubility of magnesium in aluminum, the X-ray spectrograms for alloys with increasing content of magnesium are shown[1] in Fig. 152.   The expansion of the aluminum lattice by the increasing concentration of the larger magnesium atoms is indicated by the increasing radii of the circles, arcs of which are shown on either side of the central spot on the strips of film. If the expansion of the aluminum lattice is measured for each atomic percentage of magnesium in it the result may be shown as in Fig. 157.   In determining these changes in parameter, the various alloys containing from 0 to 24.05 per cent magnesium, shown by crosses in Fig. 157, were sealed in glass tubes and heated in boiling sulphur (445°C.) in $1\frac{1}{2}$ days, to get a statistically uniform distribution of magnesium atoms throughout the aluminum lattice, then quenched in water, thus preserving in solution

[1] and SIEBEL, *Z. Metallkunde*, July, 1931, p. 202.

all of the magnesium present in each alloy, up to the saturation point at 445°C. The alloys containing 16.8 per cent and more of magnesium all showed the same parameter, indicating that no more magnesium could be dissolved in aluminum at 445°. Those containing lower percentages of magnesium—as, 2, 4, 6, 8, 10, per cent—showed a parameter proportional to the amount of magnesium present. They were unsaturated at 445°C.
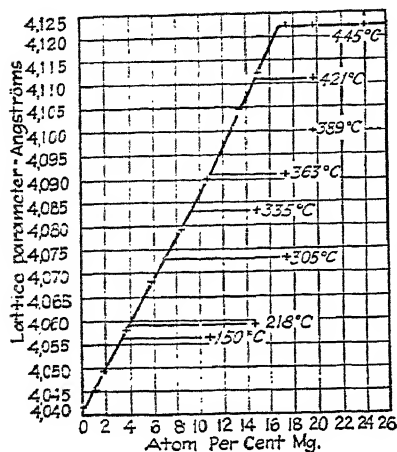
Fig. 157.

Fig. 158.

Fig. 157.—Expansion of the aluminum lattice per atomic per cent of magnesium in solution. (*Schmid and Siebel.*)
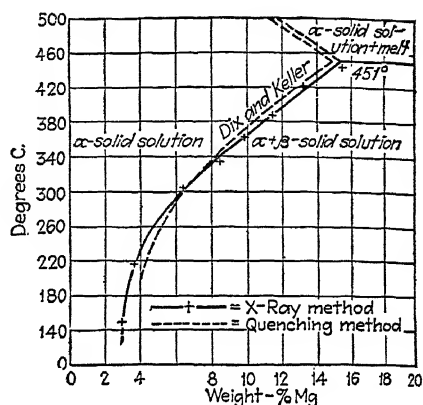
Fig. 158.—Solid solubility of magnesium in aluminum by two methods.

The expansion of the original aluminum lattice for each percentage of magnesium was then measured in each quenched alloy and is shown in Fig. 157. The aluminum lattice expands practically linearly with increase in magnesium content at the rate of 0.0047 Å. per atomic per cent of dissolved magnesium up to a limit of about 16.8 atomic per cent Mg (15.3 weight per cent)[1] at 445°C. as shown in Fig. 157. This part of the investigation could not, of course, have been done microscopically.

Once the relation is known between lattice parameter and concentration of the solid solution, it is easy to determine the solid-solubility line. It is only necessary to anneal a specimen containing 15.3 per cent or more of magnesium at various temperatures up to the eutectic temperature, quench it from each temperature, and determine the lattice parameter for the solid

[1] For the calculation of atomic per cent see footnote, p. 202.

solution existing at that temperature (in the first step all alloys were heated to the same temperature, 445°C.). The corresponding solubilities can be read from Fig. 157. The partial diagram of the system Al-Mg is shown in Fig. 158.

The older method for determining this curve was used by Dix and Keller[1] for these alloys. In the microscopic method (described on page 165) each alloy is quenched from a series of temperatures. If the microstructure of a particular alloy shows two phases when quenched from a certain temperature, the solubility at that temperature has been exceeded. If one phase only is found, it is quenched next time from a slightly lower temperature. Finally, a precipitate very small in amount is just visible at high magnification. The solubility limit lies between the last two temperatures tried for this alloy. It is interesting to note in Fig. 158 that the results obtained by the two different methods were in good agreement.

Thus, the X ray is quite useful for investigation of unsaturated solid-solution alloys where there is a consistent and measurable change in lattice parameter. Although it has not yet led to a solution of the age-hardening problem, it has been of very great value in studying alloys of the type, such as duralumin. Its use may be expected to increase steadily, although always within certain boundaries.

Diffusion in Solid Metals.—The migration of atoms through a solid metallic lattice is known as *diffusion*, and it is one of the important phenomena encountered in the physics of metals. As first proposed by Guillet in 1914, it is necessary for a solid solution to form before diffusion can take place, for if there were no tendency for a solute atom to be incorporated into the solvent lattice, diffusion could not occur. Two metals that form a series of phases with each other will thus diffuse into one another, with the formation of alloy layers equal to the number of phases stable in that system at the chosen temperature. Thus when Cu and Zn are brought into intimate contact at 400°C., they will form layers of α, β, γ, ϵ, and η phases.

Figure 159b shows a hypothetical diffusion penetration curve for the system A-B (Fig. 159a) at temperature (t). Heterogeneous fields do not appear in diffusion in binary systems. The formation of a new phase by diffusion proceeds with the inward

[1] *Am. Inst. Mining Met. Eng. vs. Engrs.*, 1929.

growth of columnar grains much in the same manner as columnar grains grow inward from the ingot sides where the first nuclei are precipitated in casting.

The diffusion that takes place between cores and encasements of a solid-solution alloy, as described on page 162, is an important example of this phenomenon.

In cases where solid solubility decreases with temperature, as in the Cu-Al series (see page 366, Fig. 277), it is necessary, if equilibrium conditions are to be satisfied, that the excess phase be precipitated as the temperature drops. The precipitating atoms migrate by the mechanism of diffusion to the phase
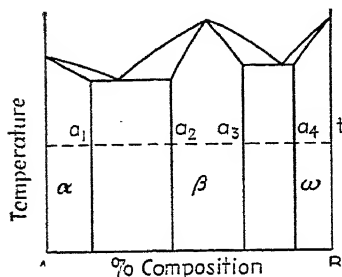
FIG. 159a.—Equilibrium diagram for the system *A-B*.
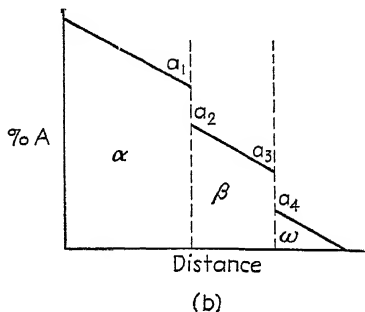
FIG. 159b.—Diffusion penetration curve for the system *A-B* at temperature *t*.

interface where they are precipitated. The quenching of such alloys to a temperature sufficiently low to inhibit the diffusion and precipitation of the low-temperature phase (except as desired) forms the basis for most heat-treatment operations, as we shall see in the next chapter.

A further example of diffusion is its utilization in obtaining an alloy surface with certain desirable properties. Thus C or N_2 may be caused to diffuse into steel to obtain surface layers high in carbon or nitrogen to give extremely hard and wear-resistant surfaces. Cr, Zn, and Al may also be caused to diffuse into the surface of steel to give corrosion-resistant properties.

Diffusion is frequently encountered when it is not desired. Brass heated to high temperatures loses Zn by its diffusion to the surface and subsequent vaporization. Steel heated in oxidizing atmospheres is subjected to decarburization by reaction of C with the gas. Gaseous H_2 diffuses into Cu, reacts with

Cu_2O present (usually in the grain boundaries) or with dissolved O_2 to form H_2O. Such a reaction results in intercrystalline weakness.

The basic relationships in diffusion were formulated by Fick as follows. The quantity of substance dS in grams that passes in time dt through cross section q under a concentration gradient dc/dx (*i.e.*, a concentration c of the cross section at a point x and one of $c + dc$ at $x + dx$) is

$$dS = -D \cdot q \frac{dc}{dx} \cdot dt.$$

D is a constant for a given substance and may be termed the *diffusion coefficient*.

As was stated in Chap. I, the lattice points in a metal must be regarded only as centers of oscillation of the atoms themselves, the amplitude of the oscillations depending on the temperature. This condition results in the possibility of an actual interchange of atoms on the lattice points and consequently presents a mechanism by which diffusion can take place. If the solid solution formed is of the substitutional type, the foreign atoms occupy the normal lattice points and diffusion takes place by participation in the normal interchange of atoms. If it is of the interstitial type, the atoms migrate through the lattice interstices. In deriving a more basic equation than that of Fick given above, Dushman and Langmuir assumed that an atom must possess a minimum energy E before it can surmount the normal potential barriers of the lattice and participate in this interchange, and on the basis of an analogy between that situation and chemical reaction rates derived the following useful formula

$$D = \frac{Q}{Nh} \cdot \delta^2 \cdot e^{-\frac{Q}{RT}}$$

where R is the gas constant, Q is the activation heat of diffusion, N is Avogadro's number, h is Planck's constant, and δ is the interatomic distance.

The most stable condition to be encountered in a solid solution is that in which the solute atoms are statistically evenly distributed in the solvent lattice. In this condition the solid solu-

tion is in its lowest free-energy state. As the solution always tends to approach its lowest free-energy state, it follows that the diffusion of solute atoms in the solvent lattice always tends to proceed from the more concentrated to the less concentrated portions of the lattice.

With respect to the *rate* of diffusion, it has been shown by experiment that as the relative difference in the size of the solute and the solvent atoms increases, the rate of diffusion increases, the slowest rate being encountered in self-diffusion where radioactive isotopes of a metal diffuse through a normal crystal of the same metal. The rate of diffusion also increases with increase in concentration gradient and with increase in temperature. Such facts lead us to suppose that the presence of solute atoms distorts the solvent lattice and decreases the magnitude of the periodic lattice forces that must be overcome for the transfer of atoms to take place, thus facilitating that transfer.[1]

Increased temperature increases the amplitude of atomic oscillation and thus facilitates the transfer of atoms and increases the rate of diffusion. Cold work, which decreases the density of the metal and increases its internal energy, so disrupts the internal periodic field of force of the lattice that diffusion is facilitated. In connection with this consideration, we would expect that the rate of diffusion through grain-boundary material, which is generally accepted as being distorted should be higher than through the grains themselves. Consequently, fine-grained specimens with more grain-boundary material should exhibit higher rates of diffusion than coarse-grained materials. In some metallic systems this is true, the diffusion of Th in W being the best example. Here the rate of diffusion in the grain boundaries is approximately 100 times that in the body of the grains. However, in the diffusion of C or N_2 into steel, no such effect is noted. In this case it may be that the higher rate of grain-boundary diffusion is obscured by intergranular inclusions, or that such a phenomenon may be characteristic of interstitial solid solutions.

[1] For further consideration of this subject, the student is referred to "Metals," Sir H. Carpenter and J. M. Robertson, Cambridge, 1939, pp. 309–411 and to R. F. Mehl, "Diffusion in Solid Metals," *Trans. Am. Inst. Mining Met. Engrs.*, Institute of Metals Division, 1936, pp. 11–56.

The diffusion of gases into metals is of the interstitial type, and the gas must diffuse in the atomic state. The gas diffusion proceeds from a film adsorbed on the metal surface, and the diffusion rate increases with temperature and pressure.

Summary.—Thus we see that the simplest type of solid solution is one in which the foreign atoms replace the native atoms in the host lattice. The three principal factors governing the extent of solid solubility in this type are (1) the size factor, (2) the electronegative valency effect, and (3) the relative valency effect. Complete solid solubility is possible only between two metals following the same crystal habit. A periodic distribution of the solute atoms is called a *superlattice* and has specific properties.

Intermediate constituents usually form in more complex lattice types and exhibit properties widely different from those of the constituent metals.

Interstitial solid solutions are usually found with solute atoms of small diameter and result in an alloy of higher than average density. The solution of C in Fe, which occurs in steel, is of this type.

By virtue of the fact that the solution of foreign atoms causes a linear expansion or contraction of the solvent lattice, X rays may be used to determine the limits of solid solubility.

Diffusion is governed by certain definite laws involving temperature, concentration gradient, and relative atomic size. It is a basic phenomenon and has many and important industrial embodiments.

CHAPTER VI

NONEQUILIBRIUM CONDITIONS IN BINARY ALLOYS. QUENCHING, AGING

Unstable Conditions in Alloy Structures.—In Chap. IV a system was developed for predicting the microstructure of any binary alloy when it is in equilibrium at any given temperature. Before turning our attention to *nonequilibrium* conditions in binary alloys, as we shall do in this chapter, it seemed advisable first to examine the crystal structure of binary alloys, as was done in Chap. V, so that the nature of nonequilibrium conditions could now be more fully understood. In all the changes through which we have seen that an alloy may pass in cooling—changes in solubility where precipitation or absorption of a phase is involved, or where with fall in temperature two phases unite into one (peritectic) or one phase decomposes into two others (eutectic)—the changes are accomplished by the *movement* of atoms from one position to another. As previously shown, the atoms diffuse past each other to equalize the concentration differences in cored crystallites; they segregate out of a supersaturated solid solution to form separate crystallites, as in a eutectoid reaction; they diffuse through a peritectic wall. Not only must the atoms be *mobile*, but they must have sufficient *time* for migration if the change is to be completed. All these processes will be retarded or even entirely prevented if the mobility of the atoms is suddenly and substantially decreased, or if the time for their migration is cut short. Therefore, if an alloy—as, for instance, one of the type indicated in Fig. 109— were quenched suddenly from a temperature above t_3 where complete solution exists, it is possible that none of the atoms will have time to separate from each other and form two separate phases before the temperature has been brought down to a much lower degree. At this low temperature the atom mobility may be so sluggish, *i.e.*, the rate of diffusion may be so slow, that the change is completely suspended and a supersaturated

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solution preserved at the lower temperature. The familiar examples of supercooling are those of water supercooled below 0°C., and glass, which remains a viscous liquid at room temperature. By this retarding means, called *quenching* in metallurgy, alloy z in Fig. 126c, if quenched rapidly enough from the temperature of the point f, would show a homogeneous structure of α-solid solution when it reached room temperature, there having been insufficient time allowed at the temperatures between f and room temperature for it to decompose. By this means, too, the

austenite (solid solution of carbon in γ iron) of Fig. 142 could be retained (at least partially) at room temperature; or, again, the peritectic formation of A_xB_y in Fig. 136 could be limited to a very thin wall of A_xB_y compound around the B crystallites, thus leaving an excess of liquid outside the wall to go down to the eutectic.

It is clear, therefore, that conditions existing in the alloy at a higher temperature can be retained, completely or partially, by suddenly bringing the alloy to a lower temperature. This state of suspended equi-

Fig. 160.—Microstructure of homogeneous-solid solution austenite. Note twinned grains. × 375. (*Courtesy of United States Steel Corporation Research Laboratories.*)

librium is responsible, as we shall see presently, for the remarkable properties of heat-treated steels and of many other heat-treated alloys.

Quenched Solid Solutions.—Of these suspended changes, most important is probably the particular case in which a solid solution is brought from a high to a low temperature so rapidly that the natural precipitation of dissolved material that should accompany fall in temperature cannot take place fully. Certain alloy steels lying in the γ solid-solution field of Fig. 141, if quenched rapidly, will remain homogeneous solid solutions at room temperature, as shown in Fig. 160. The dissolved atoms of carbon have had insufficient opportunity for diffusion and precipitation from the solid-solution lattice, and at room temperature they are relatively immobile.

Supercooling may result even when the rate of cooling is quite slow, owing to a low rate of nucleus formation or a low rate of crystal growth, or both of the phase that should form.   Thus, in hypoeutectic aluminum-silicon alloys, the primary aluminum crystals may fail to appear until a considerable quantity of silicon has precipitated.   Then, finally, the aluminum crystals start to form and continue to grow until the liquid is brought back to the proper eutectic concentration.   Such an alloy will show a structure of "primary" silicon crystals, "primary" aluminum crystals, and a eutectic between and around them.

FIG. 161.—Quenched brass of 45 per cent zinc content, showing homogeneous beta crystallites. (*Mathewson.*)

Rapid cooling of the copper-zinc alloys between 40 and 45 per cent zinc, from 800°C. or above yields a single homogeneous solid solution called *β brass*, as shown in Fig. 161, although the diagram of these alloys, shown in Fig. 269, indicates that at room temperature two solid solutions should be present.   In this case the α crystallites, rich in copper, have had insufficient opportunity to precipitate out of the β solid-solution lattice.   At room temperature atomic mobility is too sluggish for precipitation to take place.   When precipitation is allowed to take place, for example, by annealing, the structure is that in Fig. 145b.   Aluminum-copper alloys and many others yield similar homogeneous solid solutions if quenched rapidly from a high temperature.

Subcritical Transformation.[1]—When a phase has been brought into a region where it is unstable, for example, when pure iron-carbide austenite has been cooled below 723°C., the phase-equilibrium diagram no longer applies to it and can tell us nothing about the structure of the products formed and of the mechanism of their formation.   But the mechanism by which a supercooled

[1] See Hardenability of Alloy Steels, A.S.M., 1939, "Physics of Hardenability," R. F. Mehl.

JOHNSON, W. A., and R. F. MEHL, Inst. Mining Met. Engrs., *Tech. Pub.* 1089.

phase transforms is one of very great importance practically. Recent work has shown that the structure of the decomposition products of austenite, of the β eutectoid in the Cu-Al system, the β eutectoid in the Al-Zn system, and the "FeO"-wustite phase in the Fe-O₂ system is a result of processes of nucleation of the precipitating phase and the subsequent growth of grains from those nuclei. Those processes are of course similar to the process of nucleation and grain growth in the freezing of a liquid and to the recrystallization of a cold-worked metal, and the rates are in turn limited by the rates of diffusion of the atoms composing the precipitate.

Various stages in the nucleation and grain growth of pearlite in austenite at temperatures in the range of 600°C. are shown schematically in Fig. 162.
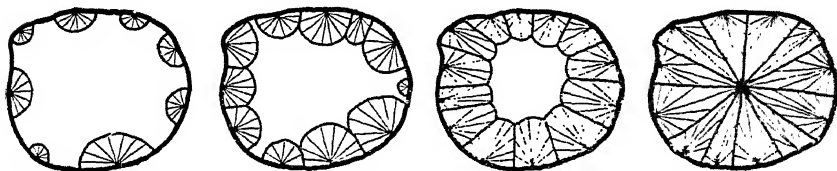
FIG. 162.—The stages in nucleation and grain growth of pearlite in austenite in the range of 600°C. (*Courtesy of R. F. Mehl.*)

In view of the fact that the rates of nucleation and grain growth vary with temperature, a specimen transforming over a range of temperatures would be expected to exhibit a range of structures.[1] In order that the transformation may be studied in its simplest aspect, it is necessary to investigate such transformations at a constant subcritical temperature where the rate of nucleation and grain growth remains constant throughout the transformation.

Davenport and Bain,[2] in a classical investigation, have determined the rates of transformation of austenite at various temperatures below its region of stability. Their results are shown in Fig. 163. On this chart about 723°C. is the lowest temperature at which austenite is stable. A group of very small specimens of eutectoid steel was quenched from above 723 into a lead bath held at a chosen constant temperature. The specimens

[1] The nature of the nuclei may change as may also the mechanism of growth.

[2] *Trans. Am. Inst. Mining Met. Engrs.*, Iron and Steel Div., 1930; *Trans. Am. Soc. Steel Treating*, November, 1932.
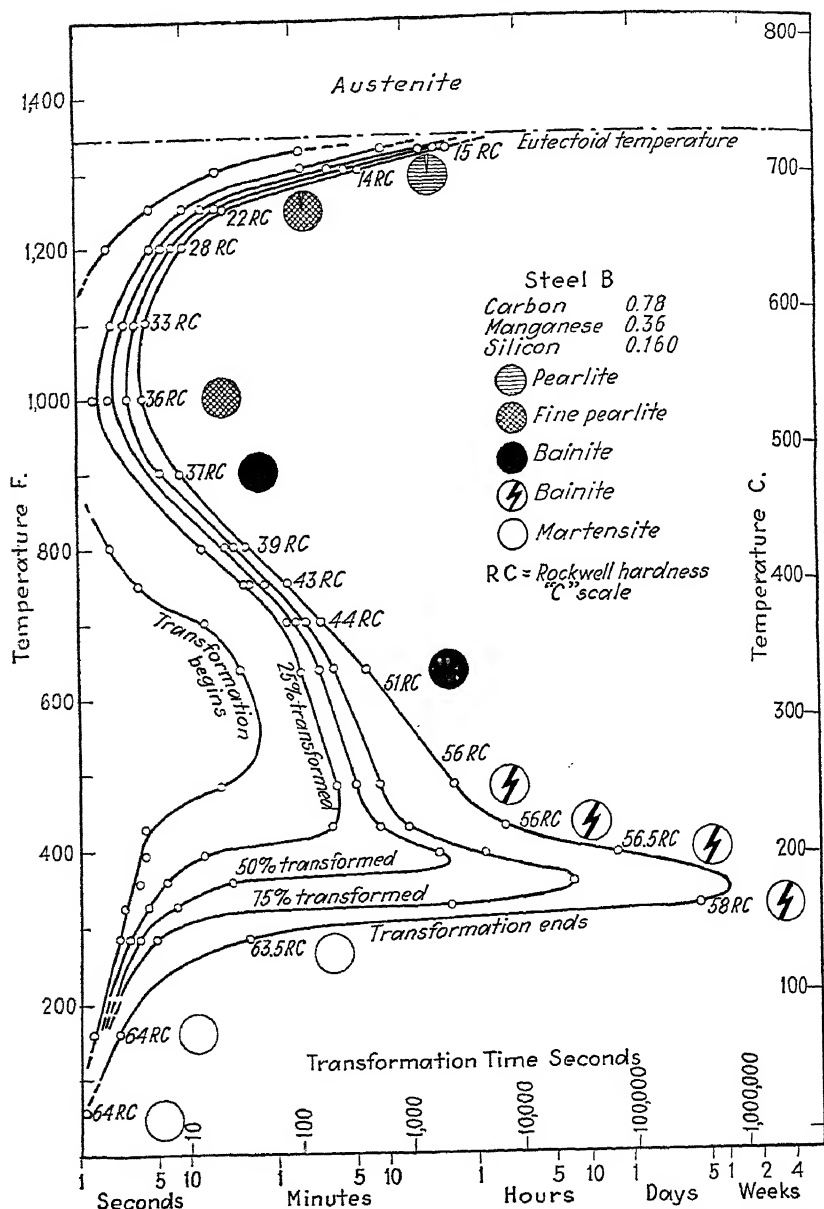
FIG. 163.—Rates of transformation of 0.78-per cent carbon steel at various (constant) subcritical temperatures. Note that the abscissae are logarithmic. (*Courtesy of the United States Steel Corporation Research Laboratories.*)

were held in the bath for various intervals of time. At the end of each interval one specimen of the group was withdrawn from the bath, quenched in iced brine, and examined under the microscope to see the extent of decomposition of the austenite that had taken place in the specimen during its sojourn in the lead bath. (Any slight degree of reaction that occurred during the brine quench could always be differentiated from that which had taken place in the lead bath at a higher temperature.) Thus the rate of decomposition of austenite at a chosen temperature
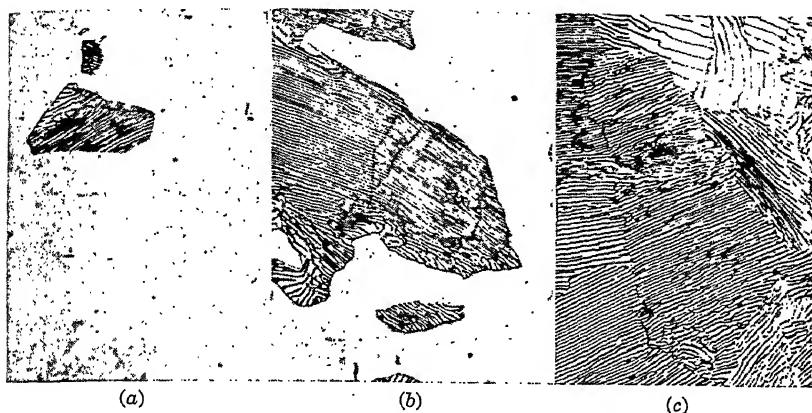
Fig. 164.—Stages in the decomposition of austenite to pearlite at 1300°F., (a) after 500 sec., (b) after 1,300 sec., (c) after 3,000 sec. (*Courtesy of United States Steel Corporation Research Laboratories.*)

was measured; *i.e.*, the rate of attainment of equilibrium in the austenite at that temperature was determined. For example, Fig. 164 shows the progress of austenite decomposition into pearlite at 1300°F. at intervals of 500 sec., 1,300 sec., 3,000 sec. after it was removed from the temperature region of austenite stability. It shows the rate of attainment of equilibrium at 1300°F. A similar group of specimens was held at each of a number of lead-bath temperatures until the rates of decomposition at all temperatures from 723° down to room temperature had been explored. The results of these measurements are plotted in Fig. 163, page 220. A series of micrographs is shown in Fig. 165.

These results obtained with iron-carbon alloys are reproduced here as a typical illustration of the rate of attainment of equilibrium in a supercooled phase, when quenched to, and held at,

various temperatures. Similar results have been found by C. S. Smith for the copper-aluminum alloys.[1]

1325°F. for 7200 sec. *RC* = 7	1300°F. for 600 sec. *RC* = 15	1250°C. for 30 sec. *RC* = 22
1200°F. for 10 sec. *RC* = 28	1100°F. for 5 sec. *RC* = 33	1000°F. for 5 sec. *RC* = 36
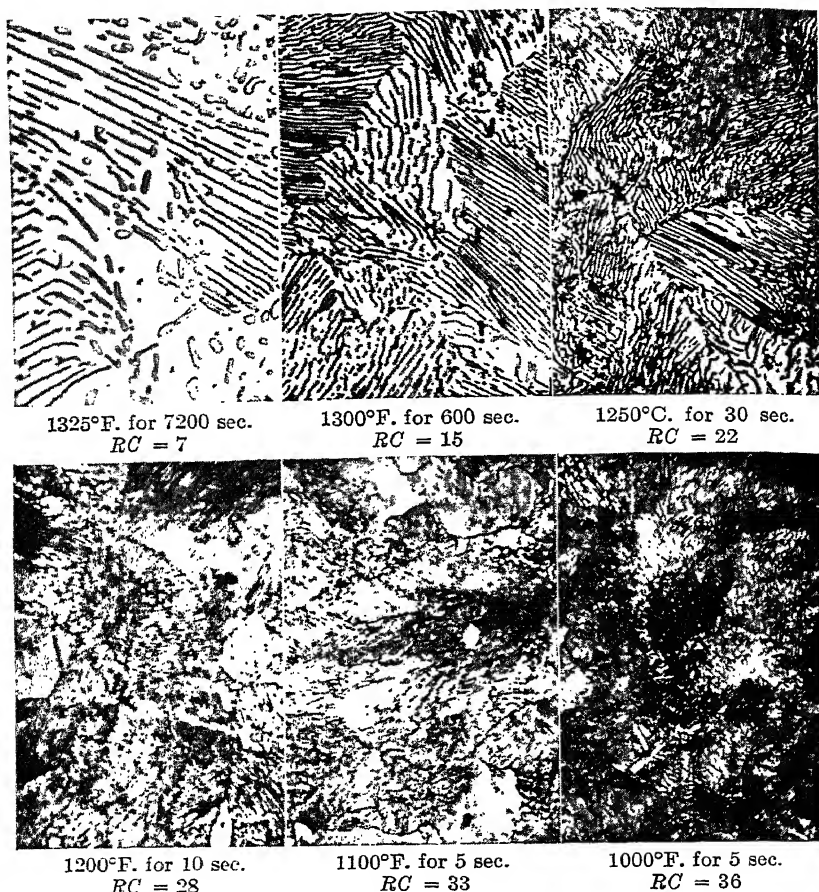
Fig. 165.—Pearlites formed by the decomposition of austenite at various (constant) temperatures, × 3,000. Note the rapidity of the reaction at the lower temperatures. *RC* = hardness on Rockwell *C* scale. See also Fig. 163. (*Courtesy of United States Steel Corporation Research Laboratories.*)

The effect of grain size on the rate of attainment of equilibrium is shown schematically, for the case where nuclei form only at the grain boundaries (temperature in the range of 600°C.) in Fig. 166. The rate of nucleation and grain growth are assumed constant throughout the transformation. It can easily be seen

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[1] *Trans. Am. Inst. Mining Met. Engrs.*, Inst. of Metals Div., 1933.

that the *rate of attainment of equilibrium* is more rapid in the small-grain-sized specimen, even though the rate of nucleation and grain growth in each grain is the same. Decreasing the grain size would thus be expected to shift the curve in Fig. 163 toward the left.

The effects of increased rate of nucleation and increased rate of grain growth are represented schematically in Figs. 167 and 168, respectively. It can be shown mathematically that variation in
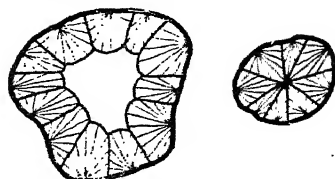
FIG. 166.—The effect of grain size on the rate of attainment of equilibrium. (*Courtesy of R. F. Mehl.*)

the rate of grain growth has a much greater effect on the rate of transformation than variation in the rate of nucleation.
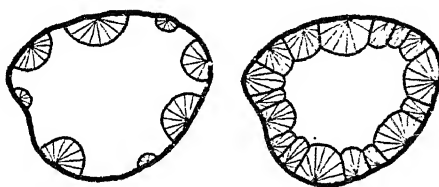
FIG. 167.—The effect of increased rate of nucleation on transformation rate. (*Courtesy of R. F. Mehl.*)

Theoretical Aspects. *The General Case.*—The first attempts to analyze isothermal reaction rates were to relate them to the isothermal rates of first order chemical reactions. Such analyses,
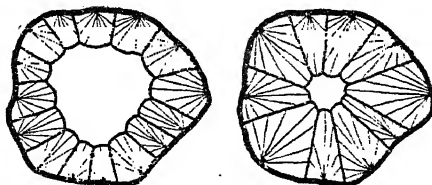
FIG. 168.—The effect of increased rate of grain growth on the rate of transformation. (*Courtesy of R. F. Mehl.*)

however, have proved fruitless, and it is now recognized that they are at best little more than empirical approximations of experimental data. The true analysis must almost certainly be based on rates of nucleation and grain growth, as developed by Johnson and Mehl.

Nucleation.—As was discussed on pages 38–39, a nucleus of minimum size is necessary in order that it shall be stable and

not redissolve. In the transformation of a solid solution, such as austenite, the rate of nucleation is limited further by the rates of diffusion of the atoms forming the precipitate. At low temperatures smaller nuclei are stable and consequently the rate of nucleation tends to increase. Opposing this tendency is the lower rate of diffusion at these low temperatures, which tends to limit the opportunity for nuclei to form. At some certain temperature the rate of nucleation will reach a maximum, owing to the operation of these opposing tendencies. At temperatures above and below it, nucleation proceeds at a lower rate, owing, at high temperatures, to the larger size of stable nucleus required and, at lower temperatures, to the low rate of diffusion. With decreasing temperatures the size of the stable nucleus will decrease until it approaches atomic dimensions.

Grain Growth.—Once a nucleus of sufficient size has been formed in the solution to be transformed, it grows by means of diffusion of the precipitating atoms to the phase interface. In the ideal case, the grains grow radially from the nucleus and result in the formation of spherical grains. The rate of diffusion at a constant temperature is dependent upon the concentration gradient. If that gradient remains constant, the rate of diffusion, and consequently, the rate of grain growth, remains constant. In an isothermal eutectoid reaction, such as the constant temperature transformation of austenite to pearlite in steel, the concentration gradient remains constant because the host solution does not change composition but transforms entirely into two new phases (also of constant composition) lying side by side. Since the compositions of all the phases involved in this transformation remain constant, the concentration gradient and, consequently, the rate of diffusion and of grain growth also remain constant.

However, when a solid solution precipitates a single phase, as in the case of age-hardening alloys the host lattice is continuously depleted of solute atoms in the region around the precipitating crystals. The continuous precipitation of solute atoms from the host lattice causes a continuous variation in concentration gradient and, consequently, in the rate of diffusion and rate of grain growth. More detailed consideration of the process will show that this variation is actually such as to decrease the gradient and, consequently, the rate of grain growth.

Figure 169 is a plot of the experimentally observed per cent of austenite transformed at 600°F. *vs.* time on both a linear and a logarithmic scale. It can be seen that the transformation starts out slowly, increases to a maximum, and then decreases with time. The reasons for the shape of the curve will be discussed on the basis of the following considerations.

For the sake of clarity, certain simplifying assumptions will be made. (1) The nuclei will be assumed to form at the grain boundaries of the preexisting phase only and to be incapable of transgressing these boundaries. (2) The grains will be assumed
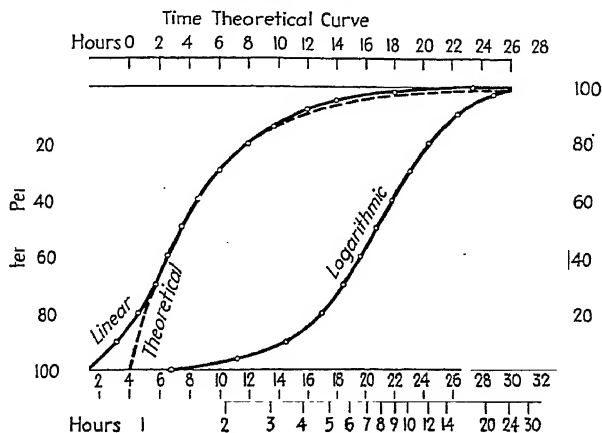
Fig. 169.—The transformation of austenite in a 3.8 per cent Mn, 0.55 per cent C steel on a linear and logarithmic time scale for comparison with the theoretical first order reaction curve. (*Courtesy of E. C. Bain and A.I.M.M.E.*)

to grow in hemispheres from these boundaries. (3) The rates of nucleation and grain growth shall be constant throughout the transformation. The initial *rate of transformation* is slow, owing to the fact that the area upon which the atoms precipitate, *i.e.*, the phase interface area, is small. This small interphase area accounts for the initial flatness of the curve. With increasing time, the phase interface area, or the surface area of the growing hemispheres increases and, although the rate of precipitation per unit area of the atoms of the transforming constituent remains constant, the overall *rate* of transformation increases. The final decrease in the *rate of transformation* is due, in turn, to the overpowering effect of the impingement of growing spheres and the consequent reduction of the phase interface area (see Fig. 162, page 219).

The Transformation Products of Austenite.—It must be remembered that not only the rate of transformation of austenite varies with change in temperature, but the products into which it transforms also depend upon the temperature of transformation. These two factors, the rate of transformation and the products of transformation, determine the results in the heat-treatment of steel.

The curve (Fig. 163) shows the rate of transformation of austenite into pearlite, increasing rapidly from a very slow rate at the equilibrium temperature (723°C.) to a maximum in the neighborhood of 550° to 570°C. The structure of the precipitating pearlite is that of increasingly finer lamellae as the temperature of transformation falls. Below 550° to 570°C. the rate of transformation decreases until a temperature of about 200°C. is reached. The transformation products of austenite in this temperature range probably do not form by a process of nucleation and grain growth, but by a mechanism of lattice alteration, which will be more fully discussed later. At any rate, in carbon steels a pearlite that can be resolved into lamellae of ferrite and cementite does not form below about 550° to 570°C. The products of transformation in the range 600° to 200°C. were first tentatively called *troostite, martensite-troostite,* and more recently, *bainite.* Below the temperature of 200°C., the rate of transformation again increases, until a second maximum is reached in the neighborhood of 150°C. The decomposition product in this range is known as *martensite.* Its formation definitely does not proceed by a mechanism of nucleation and grain growth, but by the mechanism of lattice alteration previously mentioned. Martensite is the hardest of the decomposition products of austenite, and heat-treatment for maximum hardness necessitates cooling the steel through the range of rapid transformation in the neighborhood of 600°C. down to 200° to 150°C. rapidly enough so that the austenite is essentially unchanged until the lower temperature is reached. Decomposition will then proceed with the formation of martensite only. The hardness of the decomposition products of austenite increases with decreasing temperature of transformation. The changes in structure and hardness are indicated in Fig. 163.

Lamellar Spacing in Pearlite.—In the upper temperature regions in which pearlite forms, nuclei of cementite are precipi-

tated at the grain boundaries of the austenite and the pearlite grows edgewise into the austenite, as illustrated by the direction of the arrow in Fig. 170.

The interlamellar distance of the ferrite-cementite plates decreases with temperature, resulting in the shortening of the path through which the carbon atoms must diffuse for precipitation. This shortening of the path, the absolute concentration difference remaining the same, results in an increase in the
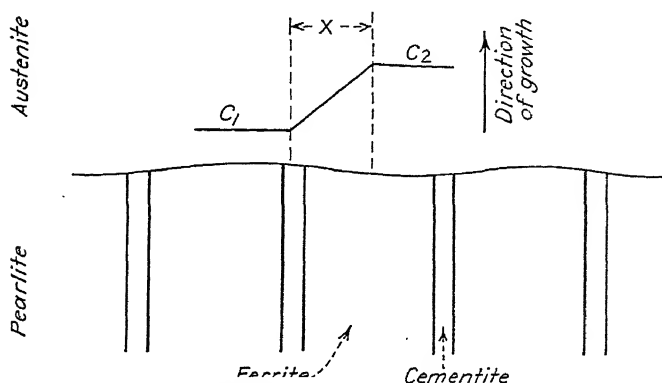
FIG. 170.—Diagram of growth of pearlite. (*Courtesy of R. F. Mehl.*)

concentration gradient. The combined effect of these two accelerating factors on the rate of decomposition of austenite evidently more than overcomes the decrease in the rate of diffusion of C in austenite with decrease in temperature, and the rate of decomposition of austenite to pearlite thus increases down to a temperature of about 600°C. The decrease in the interlamellar spacing of pearlite is linear with temperature, and if a curve plotting the log of interlamellar spacing *vs.* the reciprocal of absolute temperature is extrapolated, it is shown that pearlite will have a spacing of less than atomic dimensions at 560°C. This is obviously impossible, and pearlite must cease to form at some temperature above 560°C.

The mechanism of the formation of the intermediate phases between 600° and 200°C. will be more easily understood after consideration of the mechanism of the formation of martensite.

Mechanism of Martensite Formation.—Martensite is not, strictly speaking, a new phase, but is only a transition structure between the face-centered cubic lattice of austenite and the

body-centered cubic lattice of α iron. The mechanism of the formation of martensite was first postulated by E. C. Bain and, although oversimplified, it is essentially correct. If, as shown in Fig. 171, the face-centered atoms of two austenite unit cells are connected to the adjoining corner atoms of those cells, a distorted body-centered cubic lattice is produced. This lattice is in reality a body-centered tetragonal lattice with an axial ratio of 1.414. Now if the vertical axis is contracted and the horizontal axes are extended slightly until the axes become equal, body-centered α iron would result. However, as carbon remains in supersaturated solution in martensite, it inhibits the complete alteration of the lattice, so that the axes do not become equal but retain a final axial ratio which depends upon the carbon content. This is obviously a non-equilibrium structure and as such is extremely hard and highly unstable. Upon heating, the carbide is rapidly precipitated from solution and the final rearrangement of the lattice takes place, resulting in the formation of body-centered iron. The carbide thus precipitated is highly dispersed and not in the lamellar form.

Fig. 171.—Diagrammatic illustration of the mechanism of austenite to martensite transition. (*Courtesy of E. C. Bain.*)

Mechanism of Bainite Formation.—Speculatively, the mechanism of the formation of bainite is probably similar to that of martensite, in that the tetragonal distorted lattice forms during transformation but continuously rejects carbide from solution and takes up the α-iron lattice symmetry. The exact form of the carbide precipitation is not known, because sufficient magnification cannot yet be obtained to resolve the precipitated constituents.

However, the structures and properties resulting from the decomposition products of austenite formed at various subcritical temperatures (primary constituents) differ from those obtained when austenite is quenched drastically to room temperature and tempered. These facts are of great importance in the heat-treatment of steel.

Thus we have examined the mechanism of the decomposition in considerable detail. It may serve to illustrate the general case of eutectoid decomposition at subcritical temperatures.

Age Hardening of Quenched Alloys. In solid-solution alloys which show a decreasing solid solubility with temperature, as shown in Fig. 172, it is often possible to bring the solid solution α, *e.g.*, composition y, from the temperature interval x to room temperature so that no decomposition of α occurs en route. The alloys of aluminum with copper up to 5 per cent may

Fig. 172.—Equilibrium diagram of a hardenable alloy of hypothetical age.

be used as illustration. Figure 277 shows the constitutional diagram of these alloys with the important region enlarged. When quenched in water, after complete solution has been achieved by
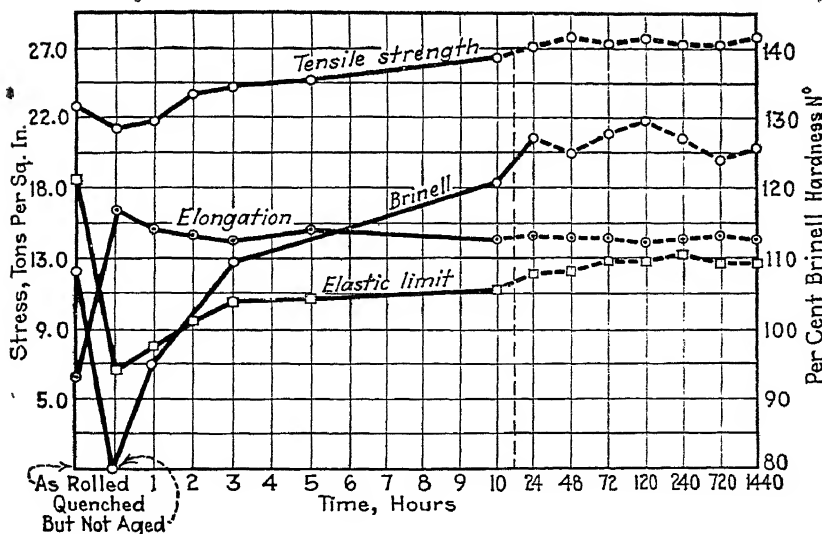
Fig. 173.—The aging of duralumin, and the changes in properties accompanying it. (*Budgen.*)

holding at 530°C., the 5 per cent Cu alloy is a homogeneous solid solution of Brinell hardness about 55 kg. per square millimeter (pure Al is 18 kg. per square millimeter). This heating and quenching is called the *solution heat-treatment*. At room tempera-

ture, after an induction period of several hours, the alloy gradually increases in hardness, at first rapidly, then more slowly, as shown in Fig. 173. Figure 173 shows at the extreme left the properties of hard-rolled duralumin sheet, then the softening following heating and quenching, and then the progressive hardening of the alloy upon standing at room temperature. Notice that the elastic limit rises from less than 7 to more than 13. The formability of the alloys decreases as the hardness and strength rise. The forming of the metal, such as bending, stamping, and riveting, is done, therefore, immediately after quenching and before hardening sets in. Aging, *i.e.*, the decomposition of this supersaturated solid solution, takes place more rapidly at 150°C. The rate of attainment of equilibrium is faster at this temperature than it is at room temperature. Holding the alloys at a definite temperature after quenching is called the *precipitation heat-treatment*. If silicon is added to the alloy, it raises the hardness, as quenched, only slightly and does not interfere with the aging process. Iron, on the contrary, interferes with aging, and, if 1 per cent iron is present, it inhibits aging.

Besides being used to advantage in obtaining high tensile properties in light alloys, age hardening is sometimes encountered where it is not desired. If maximum formability of a material is desired for fabrication processes, *e.g.*, in automotive sheet for deep drawing, the increase in power required and the liability to cracking resulting from aging are undesirable. In welding where it is necessary, in most cases, to have a ductile strong joint equal in properties to the joined material, aging is sometimes encountered. The aging in steel is probably due to the precipitation of oxide, nitride and carbide compounds of iron from a supersaturated solid solution. Any resulting brittleness of the weld is not desirable.

Theoretical Aspects.—Merica, Waltenberg, and Scott[1] offered an explanation of age hardening that greatly clarified the popular understanding of the phenomenon. They supposed that upon aging, a fine precipitate formed in the potential slip planes of the host metal, *i.e.*, in the supersaturated solid-solution crystals. Such precipitated particles, if they should obstruct slip, would automatically cause hardening. It was first proposed that

[1] MERICA, P. D., R. G. WALTENBERG, and H. SCOTT, *Natl. Bur. Standards (U.S.) Sci. Paper* 347, 1919.

very fine particles might not cause much hardening, whereas larger particles would be more effective; still larger particles were thought to fall off in effectiveness, thus explaining the usual hardness versus temperature or hardness versus period of aging curves. This supposed optimum size of particle was termed *critical particle size*. This view is scarcely tenable now. More probably it is the number of particles per unit volume that above all else determines the hardening effect, with the smallest conceivable unit of precipitate being the most effective form for any given amount of precipitation. In any event one universal feature of aging is quite clear: prolonged aging caused continued coalescence of these particles and resulted in relatively few particles of larger size, their number and disposition being insufficient to cause great hardness. The alloy was said to be *overaged*.

The process of precipitation and growth of nuclei in age hardening is generally the same as that which we have just studied in relationship to eutectoid decomposition. At solution temperature (range x, Fig. 172) the solute atoms occupy substitutional or interstitial positions in the matrix lattice. The positions are not fixed, but are, because of thermal oscillation and momentary concentration variations, continually changing by the process of diffusion. The distribution of the solute atoms is statistically such that, at any given time, groups of atoms exist throughout the matrix that are of sufficient size and proper or near proper concentration to be stable nuclei at some lower temperature. Upon quenching, these groups constitute the original nuclei of the precipitating phase. These distribution groupings may be calculated approximately by Poisson's distribution equation

$$P_{(J)} = \frac{\epsilon^J e^{-\epsilon}}{J!}$$

where P = probability of occurrence of a group, J = number of solute atoms in a group, ϵ = average number of solute atoms in a group, and e = base of natural logarithms. The necessity of a finite minimum nucleus size for it to be stable applies here, of course, just as it does in the crystallization of a liquid, as described on page 38. Schematically the size of the stable nuclei may be represented as in Fig. 174.

Once the nuclei have been precipitated, they may grow by diffusion of the precipitating atoms to the phase interface. Whereas in the isothermal decomposition of a eutectoid phase the concentration gradient and rate of grain growth remained constant throughout the reaction, here the matrix lattice, not decomposing itself, is constantly depleted of the precipitating phase, and consequently the concentration of the solute atoms, the rate of diffusion, and the rate of grain growth decrease throughout the reaction.

Aging at elevated temperatures would be expected to proceed at an increased rate because the higher rate of diffusion enables the precipitate to approach the effective number more rapidly.
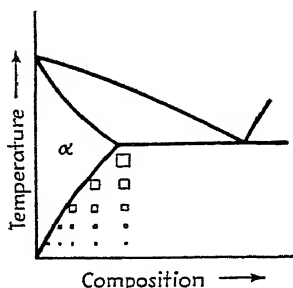
FIG. 174.—Schematic representation of the variation of stable nucleus size with temperature and composition.

When it was first proposed, many objections were presented to the simple precipitation-hardening theory on the basis of supposed anomalous changes observed in electrical conductivity, specific volume, and other properties, and on the basis that no precipitate could be detected microscopically or no change in the lattice parameter of the matrix could be detected by the very sensitive back reflection X-ray method after some precipitation had taken place. More recent work has served to demonstrate that the objections presented were not valid and that they were based upon a misinterpretation of the phenomenon rather than the inadequacy of the theory. For further reading in this interesting field, the student is referred to the bibliography at the end of this chapter.

Together with the aluminum alloys used here as an illustration, the magnesium alloys which respond to similar treatment have made possible many advances in the airplane industry and in the lightening of machine parts. The copper-beryllium alloy containing 97 per cent copper when properly aged is sufficiently hard to produce a chisel that will cut steel, and alloys containing $\frac{1}{2}$ per cent calcium enjoy an increase in fatigue life of 8,000 per cent.

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CHAPTER VII

THE STRUCTURES OF TERNARY ALLOYS
AT EQUILIBRIUM

Further improvement in the qualities of a binary alloy may frequently be gained by the addition of a third element. Nickel in steel (iron-carbon) improves its toughness, lead in brass (copper-zinc) improves its machinability, magnesium in aluminum-silicon or in nickel containing sulphur, babbitt metal, etc., are familiar examples. Fortunately, the phase rule and the
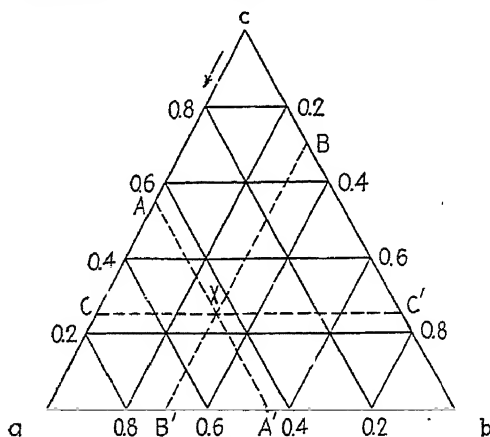
FIG. 175.—Ternary equilibrium diagram. (*Courtesy of Alloy of Iron Research of the Engineering Foundation.*)

rules for interpreting equilibrium diagrams developed in Chap. IV apply as well to ternary alloys as to the simpler binary alloys. It will be desirable, however, to point out how they apply and to illustrate their method of application.

Representation of Ternary Compositions.—If the pure components (pure metals, pure compounds, or pure nonmetallics) are represented at the corners of an equilateral triangle, *abc*, as shown in Fig. 175, then the sides of the triangles represent the bases of binary systems, *a-b*, *a-c*, and *b-c*. A point within the triangle represents a definite proportion of each of the three components. The length of each side is made equal to 100 per

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cent of each constituent as indicated. The amount of each constituent in an alloy x (Fig. 175) is determined by drawing a line through x parallel to the side of the triangle opposite the constituent. The point of intersection of that line with the side of the triangle indicating that constituent is its percentage composition. Thus the percentage a is determined by the intersection of the line AA' parallel to cb with ab and is equal to 0.45; $b = 0.30$, and $c = 0.25$.
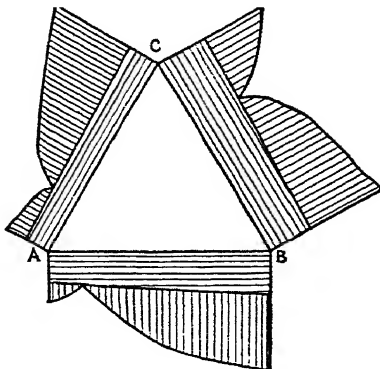
Fig. 175.—Ternary diagram showing three binary ones.

If the binary diagrams A-B, A-C, and B-C are drawn in, they might, in a simple case, appear as shown in Fig. 176. If now these three binary diagrams are stood upright, so that their vertical
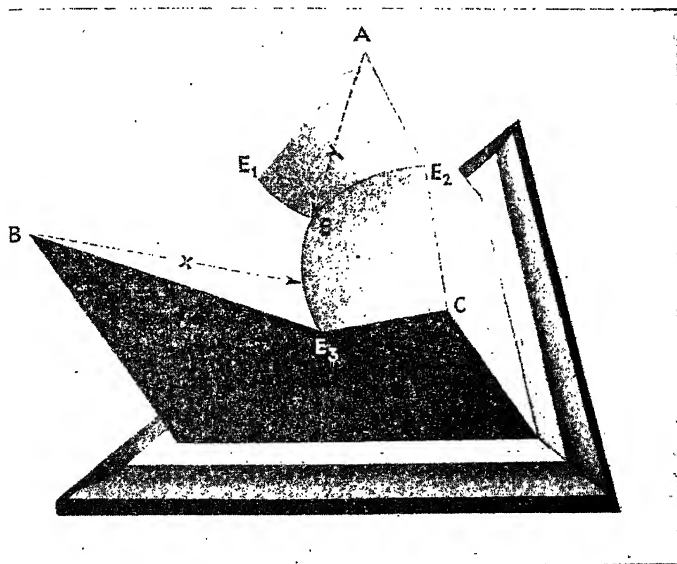
Fig. 177.—Solid model of a ternary system.

temperature ordinate is in its usual position, we have a solid figure of triangular base as shown in Fig. 177. A vertical line rising from any point in the basal triangle represents a certain

alloy at a series of temperatures.   All such lines intersect with the *liquidus surface* of irregular shape, at the top of the diagram. A solid model would thus be required to show the new diagram. A photograph of such a model is shown in Fig. 177, showing the curved liquidus surfaces or "hills," and the "valleys" between them.

Complete Solid Insolubility.   The Ternary Eutectic Reaction. An alloy of composition x in Fig. 177 would begin to precipitate crystals when its temperature had intersected the liquidus surface BE_1EE_3.   The crystals are found, by drawing a horizontal line

FIG. 178.   FIG. 179.

FIG. 178.—Structure of ternary alloy lead-tin-antimony, showing white cubes (primary SbSn) coarse eutectic, secondary, and black background, ternary eutectic.   (*Guillet.*)
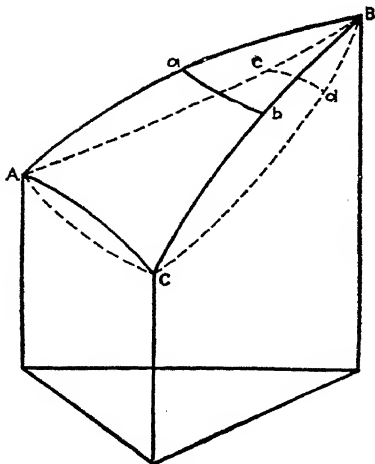
FIG. 179.—Ternary diagram of three completely soluble components.

through x and through the vertical at B, to be pure B crystals. The melt, thus impoverished in B, moves down the liquidus plane in a direction directly away from the vertical B, precipitation of B continuing until the melt reaches the line E_3E.   At this line, the liquid, previously saturated in B, is now saturated also in C and precipitates alternately B and C crystals, as a *quasi-binary eutectic*, the temperature falling gradually as the liquid moves downward along the line E_3E.   Enrichment of the liquid in A results from this deposition of B and C material, with the result that, at the point E, saturation in A is reached also.   At this point of intersection all three kinds of crystals precipitate

alternately, the temperature and the composition of the melt remaining constant until solidification is complete. This point is called a *ternary eutectic point*. All alloys of this system, chosen for illustration, complete their solidification at this temperature and composition. Hence a horizontal *plane*, within the body of the model, should be installed at this temperature. It is the *solidus plane* of the system and lies at a lower temperature than do any of the binary eutectics concerned.

The Structures of Ternary Eutectic Alloys.—The structure of such an alloy would show primary crystals, white in Fig. 178,
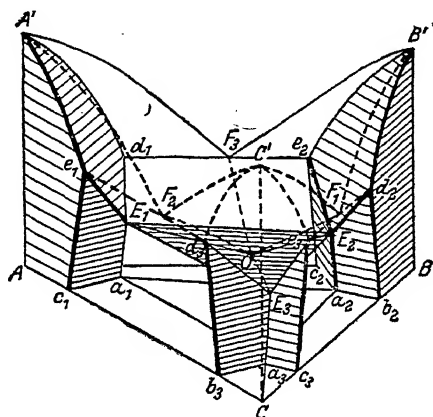
Fig. 180.—Ternary system showing partial solid solubility. (*Guertler.*)

surrounded by a quasi-binary eutectic, of crystals of B and C. The regions between this eutectic, *i.e.*, the last regions in the structure to solidify, would be regions of a ternary eutectic of A, B, and C crystals interspersed with each other.

All alloys will show the ternary eutectic, but both the primary and the secondary crystallizations will be lacking in the ternary eutectic alloy E. The secondary or quasi-binary eutectic crystallization is absent from the alloy y, as shown in the diagram. Obviously, if the x alloy had lain nearer to E_1, the secondary crystallization would have contained B and A crystallites instead of B and C crystallites. The structures of other alloys can be inferred readily from these examples.

Completely Soluble Ternary Alloys.—Completely soluble ternary alloys would be represented, similarly, by a diagram as shown in Fig. 179. This case is considerably simpler to follow.

Partially Soluble Ternary Alloys.—The case intermediate between the preceding two, namely, that of partial solubility, is shown in Fig. 180. The solid solubility at room temperature
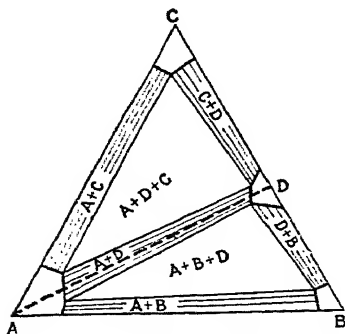
FIG. 181.—Ternary system containing a compound *D*. (*Guertler.*)
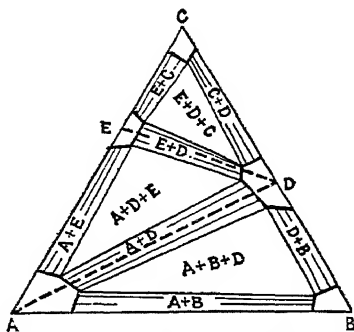
FIG. 182.—Ternary system containing two compounds. (*Guertler.*)

is shown in the enclosed areas of the "posts" at each corner of the basal triangle. Thus the solubility of C for A and B is shown by the area within $b_3Cc_3a_3$, etc. The ternary eutectic point is shown at O. The solidus plane below which no liquid exists is the plane $E_1E_2E_3$. The "posts" at A, B, and C represent the homogeneous solid-solution alloys.
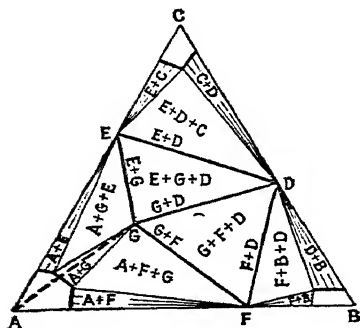
FIG. 183.—Ternary system containing four compounds. (*Guertler.*)

Metallic Compounds.—When intermetallic compounds are present in ternary systems, it is simplest to divide the diagram into parts, just as was done in the binary systems. A simple case of one compound D (or C_xB_y) in the system A-B-C is shown in Fig. 181. A line drawn from the point D to the opposite angle at A divides the system into two ternary systems C-A-D and D-A-B, each of which can be handled as a separate system. This diagram (at room temperature) shows all four components slightly soluble in each other in the solid state, as indicated by the one-phase fields at the three corners and at D. The shaded regions are, as usual, two-phase fields. When two compounds

are present, the conditions may be simplified as in Fig. 182, etc.
The absence of a line from E to B in this diagram indicates that
this quasi-binary alloy system E-B, although possible, is not real
but imaginary, at the pressure at which it was investigated.
Guertler has shown that if an alloy be prepared of composition
corresponding to the intersection of line AD with a line EB, the
alloy can (by the phase rule) show only two kinds of crystallites.
If it shows crystallites of A and D, then the system E-B is
imaginary and A-D is real. All lines crossing AD must, there-
fore, be imaginary also. The case where a *ternary compound* G
forms is shown in Fig. 183. Known ternary compounds are
Al_6Mg_4Cu, $NaCdHg$, and $NaKHg$. Others also are known.

Sections Through Ternary Model Showing Equilibrium in Alloys Containing 3%, 15% and 50% Chromium
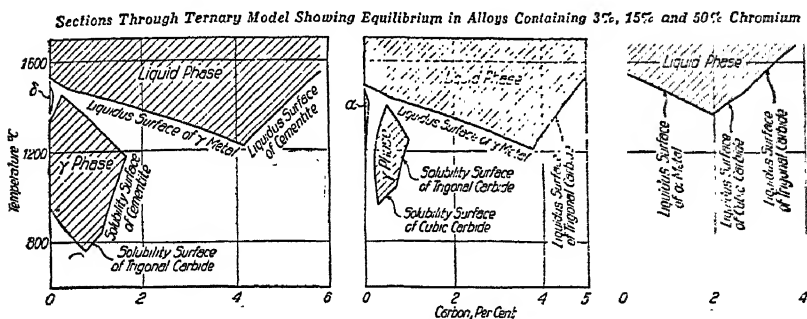
Fig. 184.—Representation of iron-carbon chromium alloys in one plane. (*Bain.*)

Sections through the Ternary Model.—Another method for
showing phase conditions in ternary alloys is to construct a
simple binary diagram with a *constant percentage* of the third
element present. This method requires, of course, a separate
binary diagram for each percentage of the third element that
is to be shown, but it has the advantage of being reproducible
in one plane. Such sections for the chromium steels of 3, 15,
and 50 per cent chromium are shown in Fig. 184. The disap-
pearance of the γ phase with increasing chromium and the rising
of the eutectic and eutectoid temperatures are clearly shown.
The eutectic composition decreases from 4.3 per cent carbon for
plain cast iron to 2 per cent carbon with 50 per cent of chromium.

Selected Literature

See list at end of Chap. IV.

CHAPTER VIII

THE PROPERTIES OF ALLOYS

General.—As noted at the beginning of the study of alloys in Part II, one is interested in the internal structure of alloys mainly because the mechanical, physical, and chemical properties of the alloys arise out of their internal structures.

THE PROPERTIES OF LIQUID ALLOYS

The properties of liquid metals change relatively little when foreign atoms are introduced, as compared with the change
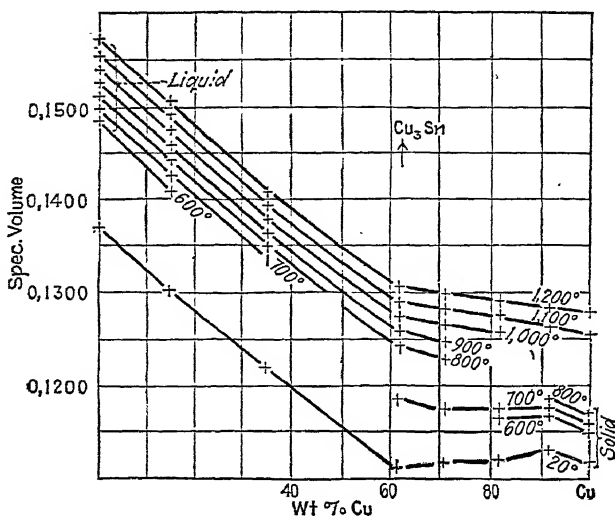
FIG. 185.—Specific volume $\left(= \dfrac{1}{\text{density}} \right)$ of liquid and of solid tin-copper alloys at various temperatures. (*Sauerwald.*)

produced in solid metals.[1] Some of the properties of liquid alloys vary linearly with the composition, whereas others do not. The specific volume of liquid tin-copper alloys varies linearly

[1] An exception occurs in the case of surface tension, *e.g.*, in type metal.

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from 0 to 62 per cent copper (Cu_3Sn = 62 per cent Cu), as shown in Fig. 185, but further additions of copper have much less effect in lowering the specific volume of tin.[1]

The viscosities of the lead-bismuth alloys are somewhat less than the linear values would be. The temperature coefficient of viscosity for any given alloy is nearly linear.[2]

The surface tension of binary alloys is almost always less than the linear average of that of the two components.[3]

The electrical conductivity of liquid alloys follows, in general, the form of curves shown later for solid solutions.[4]

It seems likely that the nonaverage properties of liquid alloys result from the presence of intermetallic compounds, molecules partially dissociated, or ionized, in the solvent metal.[5]

Properties Are Related to Structure.—If the solidified combination of two metals can result in the variety of structures such as those indicated in Fig. 116, page 159, or in Fig. 144 of Chap. IV, including a number of intermetallic compounds and solid solutions of various types, and in a variety of structural designs composed of these constituents, it is perhaps not surprising that the properties both physical and chemical which accompany them, often depart greatly from any linear relation with the total composition of the alloy as determined by a chemist. For an alloy series of two metals nearly insoluble in the solid state, a simple eutectic series, let us say, as shown in Fig. 186 for Pb-Sb, the hardness is approximately linear between the hardness of pure Pb and that of pure Sb, and varies with the proportionate weights of the two kinds of crystals present. The linear relationship is dependent to a great extent upon an even distribution of the constituents of the mixed series. If, however, one constituent is finely divided so as to form a film around the other, as in the case of small percentages of Bi in film form around Au crystals, the strength of the resultant alloy depends almost entirely upon the strength of the film-forming material. If, as in the case of age-hardening alloys,

[1] SAUERWALD, *Z. anorg. Chem.*, **155**, 1, 1926.

[2] SAUERWALD, *Z. anorg. Chem.*, **161**, 51, 1927.

[3] MATUYAMA, *Science Reports*, Tôhoku Imperial University, **16**, 5, p. 555.

[4] MATUYAMA, *Science Reports*, Tôkohu Imperial University, **16**, 4, 1927.

[5] SAUERWALD, *Z. Metallkunde*, **18**, 137, 1926; GIESSEREI, *Z. Metallkunde*, **16**, 49, 1928.

one constituent is in the characteristic highly disperse form, representing an increase in surface energy and mechanical resistance to deformation, the hardness of the alloy series would not be expected to vary linearly.   Consequently, the strength and hardness of duplex alloys, although of the greatest industrial importance, depend primarily upon the distribution and form of their components and are of little theoretical interest.
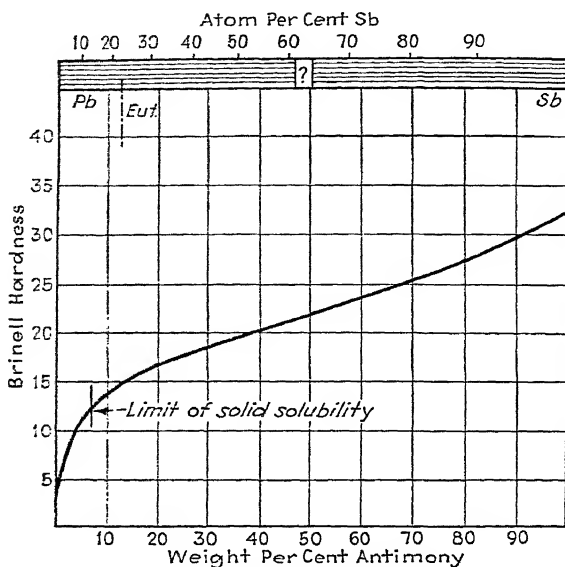
Fig. 186.—Hardness of lead-antimony alloys.

Hardness of Solid-solution Alloys.—For solid solutions, on the contrary, the hardness relations are of very great theoretical interest.   The hardness of either pure metal is increased by the introduction of foreign atoms into the crystal lattice.   The hardness rises steadily to a maximum at 50 atomic per cent of each metal, as shown for the Cu-Ni alloys in Fig. 187.   To say the least, it is surprising that the addition of the softer Cu to the harder Ni should increase the hardness of the nickel; however, upon proper reflection, the problem resolves itself into a question, not of the hardness of the individual constituents, as was the case in duplex alloys, but into a question of the effect of the solute atoms upon the solvent lattice and the nature of the lattice forces operative, owing to the interaction of different atomic species.   As we

shall see, the other properties of solid solutions, *viz.*, electrical and heat conductivity, etc., also depend upon these interactions.

As the theory of the metallic state is not sufficiently advanced to predict quantitatively the effect of distortion and of the new distribution of electrons around the metallic nuclei (due to alloying) upon the lattice forces, we must be content with a
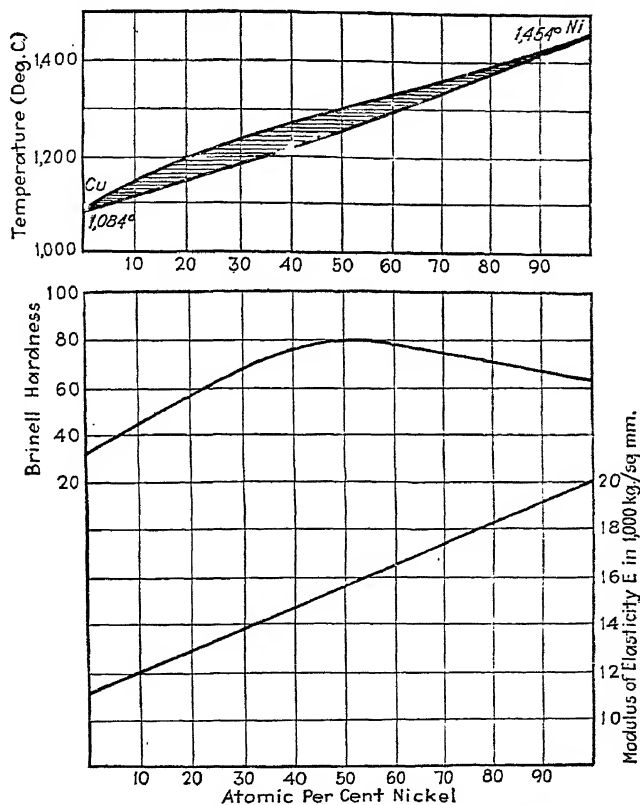
Fig. 187.—Hardness of copper-nickel alloys (also modulus of elasticity). (*Guertler.*)

qualitative outlook. We would expect that at 50 atomic per cent of each metal the lattice distortion would be a maximum and the consequent distorted periodicity of lattice forces and disrupted continuity of slip planes would be least favorable for slip. Since in alloy series not exhibiting complete miscibility solid solubility is limited by the capacity of the solvent lattice to undergo distortion in accommodating solvent atoms, the solid-

solubility limit corresponds to the maximum distortion of which that lattice is capable. Thus, sparingly soluble additions should produce great distortion and great hardness, even when present in small amounts. Table IX shows results for lead by Ludwig that seem to support this theory.

TABLE IX.—HARDENING OF LEAD ALLOYS

Added metal	Average increased hardness for 1 per cent	Solution reaches saturation at per cent
Bi	0.5	30.0
Sn	1.8	10.0
Cd	4.8	5.5
Sb	10.1	2.5
Mg	11.0	0(?)

Advantage of this increase in hardness and strength is taken in the industrial brasses, bronzes, and lead and aluminum alloys, where zinc, tin, and other elements are dissolved in the host crystallites and strengthen them; in the addition of copper to gold in jewelry and coinage, in monel metal, and also in the alloy steels, particularly as in nickel-steel, where the added elements dissolve in the ferrite or the iron lattice. The identification of the Pt-Rh wire in a thermocouple is easy if both wires are bent. The alloy wire is harder to bend than is the pure platinum one. The hardness of single crystals of solid solutions has been studied by Elam.[1]

Hardness of Intermediate Constituents.—For stable intermetallic constituents in an alloy series corresponding to definite chemical formulas, e.g., $CuZn$, $CuAl_2$, etc., the rule is that the intermetallic compound is almost without exception harder than either of the combining elements, just as are the solid solutions. But such compounds possess very little of the formability of the solid solutions and are usually very brittle, often to the point of pulverizing when stressed. We have seen that such compounds correspond to definite valence electron-atom ratios (see page 204, Chap. V) and we may consequently attribute much of their brittleness and lack of metallic properties to their tendencies to form homopolar bonds, especially when one of the elements of

[1] *Proc. Roy. Soc.* (London), **109A**, 143, 1925.

the compound is a nonmetal (*e.g.*, Fe_3C). Such compounds are usually high melting and retain their high hardness to quite high temperatures. A very small portion of a metallic compound will often lend stiffness and rigidity to an otherwise soft and yielding metal, such as, for instance, Fe_3C in ductile iron, $CuAl_2$ in soft Al, etc. Tungsten and tantalum carbides, which are high melting and extremely hard, are useful in high-speed tool steels for cutting purposes. It is because of the preponderance of such compounds, however, that certain alloys of the ductile metals copper and aluminum are, surprisingly enough, almost as brittle as glass, namely, those certain alloys in which a compound of copper with aluminum (CuAl) or $CuAl_2$ predominates. The compounds of iron with nitrogen are formed in the process of nitriding steel to form a hard surface (see Fig. 236, Chap. X). The hard particles of SbSn in babbitt bearing metal support the moving part. They are set in a soft matrix.

FIG. 188.—Schematic variation of hardness with composition of alloys including solid solutions, a chemical compound, and aggregates of both.

Thus the hardness of intermetallic compounds finds great usefulness in stiffening or strengthening a metal background or matrix that is too soft and ductile or in providing a hard, wear-resisting surface or sharp particles for cutting. In other cases, however, the brittleness that accompanies the hardness limits the use of these compounds.

The Hardness of a Whole Series of Alloys.—Knowing the hardness behavior of (1) solid solutions, (2) of metallic compounds and (3) of aggregates or mixtures of any two of these in a single alloy, we are ready to examine the hardness of a complete series of alloys in which all of these constituents may be present. In Fig. 188, for illustration, the hardness of pure A rises rapidly

as long as the A lattice can take material containing B atoms into solid solution. A_xB_y shows its characteristic high hardness value. Mixtures of saturated A solid-solution crystals and A_xB_y crystals have hardness proportional to the amount of each one present, as shown by the straight line connecting the hardness figures of the two. From A_xB_y to saturated B the hardness drops steadily with increase in the amount of the softer B solid solution present in the alloy. In this series the hardness of the entire alloy system may be plotted if the hardness of pure A, pure B, of pure A_xB_y, and of the saturated solutions of A and of B is known.

While these rules do not pretend to apply with exactness or in every case, owing, for instance, to disturbing secondary conditions that may obtain, yet they do form a logical basis for judgments of the kind that are most frequently needed in both scientific and engineering work.

The Formability of Binary Alloys.—Alloying usually reduces the formability of the pure metals, although not so far but that both solid solutions and insoluble aggregates remain industrially useful (provided metallic compounds are not predominant).

Duplex Alloys.—Insoluble additions, as sulphur in iron or in nickel may, however, form brittle envelopes of sulphides around each grain destroying completely the formability of the alloy. Thus 0.01 per cent of sulphur in electrolytic iron renders it entirely brittle both when hot and when cold, because of the softening of the envelopes when hot, the brittleness when cold. If manganese is added to the melt it combines with the sulphur in the iron and forms tiny *globules* of MnS which thus collect the sulphur and eliminate the grain-boundary brittleness. Similarly, 0.01 per cent sulphur in nickel forms an alloy so brittle that it will fly to pieces if struck by a hammer, owing to films of a solid solution of Ni and Ni_2S_3 at the grain boundaries. The addition of 0.05 per cent magnesium to the melt converts the sulphur to magnesium sulphide of high melting point and relatively insoluble in nickel which collects in tiny globules and leaves the formability of the nickel unimpaired. Similarly 0.005 per cent of lead renders gold brittle due to a gold compound at the grain boundaries. On the other hand, steel, containing, as it does, the brittle iron carbide in intimate association with the ductile ferrite in pearlite, is ductile up to some 0.70 per cent carbon and highly ductile

in the lower carbon ranges. The ductility may be attributed to continuous paths for deformation through the ductile ferrite.

Thus the location and form of the constituents of an aggregate play very important parts in determining the formability of the metal. The influence of a brittle constituent is very much lessened when it is dispersed throughout a continuous plastic phase than when it occurs in continuous envelopes at the grain boundaries.

Solid Solutions.—The ductility of solid solutions is often greater than that of the pure components of the solution, for drawing them through a die strengthens them rapidly and thus permits further reduction in size without breakage. The force required to cause deformation is, however, always higher than it is for pure metals. The rapid hardening of solid solutions upon deformation

FIG. 189.—Formability of brass.

is illustrated in the stamping of stainless steel for automobile headlights. Fine-grained metal usually has better formability than coarse-grained metal.[1]

An interesting example of the formability of alloys may be taken from the Cu-Zn system. The formability of brass is plotted as ductility vs. atomic per cent Zn in Fig. 189 (Stillwell). It may be seen that α brass has a characteristic high formability, while the intermediate constituents are very brittle. In making band instruments, those parts that must be shaped are made of the ductile, strong α brass solid solution. However, the keys in the instrument must be hard to resist wear, and rigid to retain tone. The keys, consequently, are cast from γ brass corresponding to a composition of Cu_5Zn_8, which is hard and wear resistant, thus excellently meeting the service requirements.

The Specific Gravity of Alloys.—The specific gravity of an alloy composed of a conglomerate of two kinds of crystallites is not proportional to the specific gravity of each crystallite present. But the reciprocal of the specific gravity; *i.e.*, the *specific volume* is quite closely so proportional. The specific volume V of a given alloy containing n per cent by volume of A crystallites and

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[1] Grain size and properties of steels are discussed on page 349.

100 − *n* per cent by volume of *B* crystallites is equal to

$$nV_A + (100 - n)V_B$$

The reciprocal of this sum gives the specific gravity of the alloy considered.

This same rule holds very closely for solid-solution series, although there may be slight contraction in volume (less than 0.5 per cent) causing a lower value than calculated. The deviation in solid-solution alloys is reflected in lattice parameter measurements. The lattice parameter relationship departs slightly from linearity, owing to the distortion that results from alloying. Figure 190 shows the variation in lattice parameter in
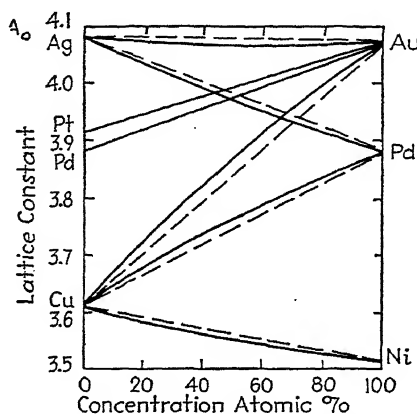
Fig. 190.—Variation of lattice parameter with composition of several alloy systems. (*Courtesy of C. H. Johansson.*)

several solid-solution series. The specific volumes of the copper-tin alloys are shown at several temperatures in Fig. 185.

The specific volumes of intermetallic compounds deviate somewhat from this rule, but owing to the small proportions of such compounds present in engineering materials, the above rule may be used with a satisfactory degree of accuracy.

Thermal Expansion.—For duplex alloys the thermal expansion may be calculated by the law of averages from the coefficient of the respective constituents of the alloy by the formula

$$\alpha_{(a+b)} = n\alpha_a + (100 - n)\alpha_b$$

The specific gravities and coefficients of thermal expansion for the pure metals are given in Table III, pages 60 to 63.

While each alloy in a duplex series has a cubical expansion in linear ratio to its composition, the same is not necessarily true for solid-solution alloys, although it is approached in some cases. Figure 191 shows the variation in the coefficient of expansion with
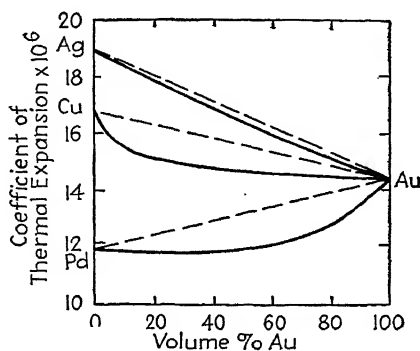
FIG. 191.—Variation in thermal coefficient of expansion with composition in several alloy systems. (*Courtesy of C. H. Johansson.*)

composition for the solid-solution alloy systems of Ag, Cu, and Pd with Au.

The most interesting and useful solid-solution systems with respect to thermal expansion are those of the ferromagnetic metals. Evidently the factors that give rise to the ferromagnetic
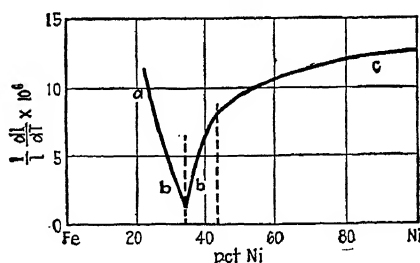
FIG. 192.—Coefficients of expansion of iron-nickel alloys.

nature of the alloys so complicate the changes in the expansion coefficient that the theoretical reasons for those changes are difficult to determine. However, this circumstance in no way detracts from the usefulness and interest that arise from the wide variation in expansion coefficients obtainable in these systems. Guillaume investigated the thermal dilation of Ni iron alloys. Ni steel with 36 per cent Ni has a vanishingly small thermal expansion, as shown in Fig. 192. Invar, an alloy of this com-

position, because of its negligible coefficient of expansion, finds use in the manufacture of scales, pendulums, surveying tapes, etc., and as struts in Al automobile pistons, to adapt the expansion of the piston to that of the cast-iron cylinder. The alloys of 53 per cent Ni have the same coefficient of cubical expansion as glass and are used at the seal in incandescent lamps instead of the former more expensive platinum, which also has a coefficient of expansion the same as glass. Alloys may be made to match the coefficient of expansion for tungsten or glass of any composition. The addition of 8 per cent Ni and 18 per cent Cr to low-carbon steels increases its coefficient of expansion some 20 per cent in the range from 20° to 700°C. This increased expansion gives excessive warping in the welding and heat-treatment of stainless steels. Iron alloys of high coefficient of expansion, such as 17 per cent Ni, 11 per cent Cr or 23 per cent Ni, 5 per cent Cr, are used with Invar as components of bimetallic strip for industrial temperature control. In view of the complexity of the influencing factors, no general rule can be given for the thermal expansion of solid solutions.

The Specific Heat of Alloys.—Neumann in 1831 and Kopf in 1865 advanced the hypothesis that in a binary alloy composed of two metals whose atomic heats were C_1 and C_2, the atomic heat of the alloy may be calculated from the formula

$$C_{a+b} = p \cdot C_1 + q \cdot C_2$$

where p and q are the gram-atomic per cents of the components. The law was first formulated without knowledge of the various structures in which the constituents of binary systems may solidify. However, the law has been proved to be generally valid for all types of alloys that we now know: duplex alloys, solid solutions, and intermetallic compounds.

The Melting Point of Alloys.—The melting and freezing range of alloys is, of course, given in the constitutional diagram of each alloy series. The importance of many alloys depends mainly upon their melting points; for example, in fuse metal, type metal, solder, and fire-protective safety devices. These safety devices depend upon the melting of an alloy plug to start a sprinkling system. In most of the cited cases, the low-melting-point metal is usually a eutectic mixture.

The Color of Alloys.—If a gray metal is alloyed with copper or gold, the natural reddish colors will, when sufficient gray metal has been added, gradually disappear. For example, the gray color first appears in copper when 20 per cent palladium, 23 per cent nickel, or 22 per cent manganese has been added, smaller additions revealing a yellow or yellowish gray tint. Forty per cent platinum, 19 per cent aluminum, or 50 per cent zinc produces the same effect.

Gold, likewise, gradually loses its color as the amount of gray metal in solid solution is increased. Below 65 per cent gold, the gold-silver alloys are a greenish yellow. Below 30 per cent gold they are white.[1] Gold is colored gray by the addition of 5 per cent of tin or 4 per cent of bismuth.

The Electrical Conductivity of Alloys.—The resistance r of a metallic conductor is directly proportional to its length l and inversely proportional to its sectional area q, or

$$l$$

If $l = 1$ cm. length, and $q = 1$ sq. cm. sectional area, then $r = \rho$; the resistance of a symmetrical cube, whose edges are each 1 cm., is called the *specific resistance* of the metal, and its reciprocal value is called the *specific conductance* or *conductivity*. Thus it is the volume of a conductor, not the weight, with which one is concerned. The electrical conductivity of the pure metals is given in Table III, pages 60 to 63.

Duplex Alloys.—When an alloy series is composed of two kinds of crystallites, the conductivity of any particular alloy will be almost proportional to the *volume* of each variety of crystallite in the alloy and to the specific conductance of each variety (assuming a random orientation with no fiber structure). Just as we can imagine a bar built up of alternate uniform blocks of iron and copper, the conductance of the bar would depend rather on the total *volume* of each metal present than on the *weight* of each metal present. While this relationship holds rather accurately for the tin-cadmium alloys, as shown in Fig. 193, the conductivity is slightly lower than that calculated for alloys of zinc-cadmium and lead-cadmium.[2] Obviously, if a continuous

[1] TAMMANN, G., "Textbook of Metallography," p. 280, Chemical Publishing Company, Inc., New York, 1925.

[2] FRY, *Z. Elektrochem.*, May, 1932, p. 260.

oxide film enveloped each grain in an alloy, the conductivity would be very low, oxides usually being high in dielectric strength.

Solid Solutions.—The conductivity of pure metals drops astonishingly when even a minute quantity of a second element
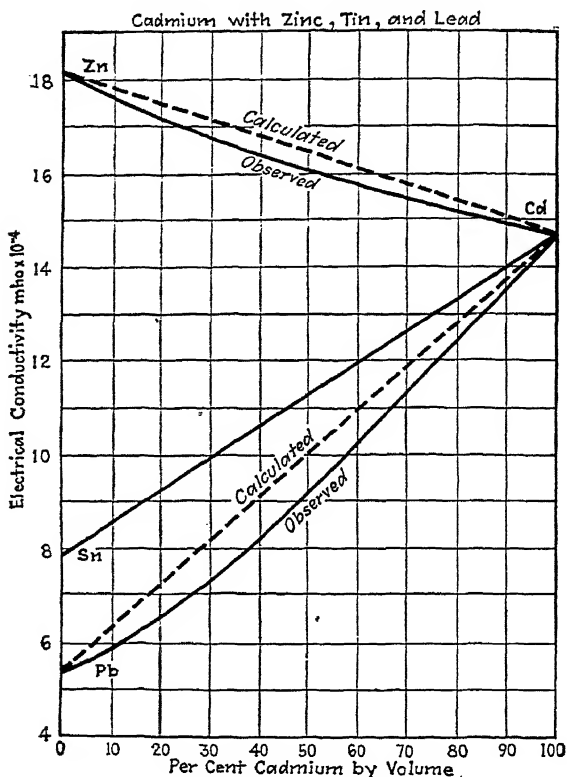
Fig. 193.—Electrical conductivity of some cadmium alloys.   (*Guertler.*)

is dissolved in its crystal lattice, *i.e.*, when a solid solution is formed.   Figure 194 shows the conductivity of the alloys of gold and silver.   The conductivity curve takes the form of a catenary. (Not, however, like a chain uniformly loaded and hanging between two points, but like a chain whose loading decreases as the distance from its supports increases, or like two black-snake whips hung up by their handles and with the lashes tied together.)   The increase in resistance may be attributed to the various factors disrupting the free transfer of valence electrons through the lattice.   Norburg, in noting the effect of 1 per cent

of various elements added to pure Cu, Au, and Ag, found that the resistance due to any given metal was greater, the greater the distance between the solvent and solute in the periodic chart. Upon consideration of that statement, it might be said also that the greater the valence of the solute, the greater is the increase in resistance.[1] Linde has shown that in the addition of 1 per cent of C, In, Sn, or Sb as a solute to Ág, the resistance varies as $(V - 1)^2$ where V is the valence of the solute and, of course, 1 is the valence of Ag.
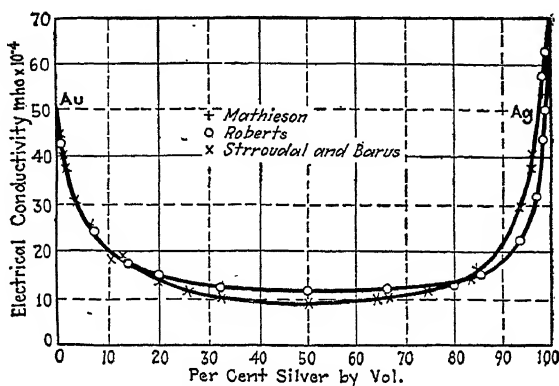
FIG. 194.—Conductivity of gold-silver alloys.

With this rapid fall in conductivity near the pure metals, we at once appreciate why the electrical industry demands copper of very high purity. For example, absolutely pure copper has a conductivity of 64×10^4, while 99.95 per cent pure copper has only 56×10^4 reciprocal ohms per centimeter cube. This 0.05 per cent of impurity has decreased the conductivity by more than 12 per cent. Furthermore, a drop is caused even if the metal added be a very good conductor. Even a good conductor like copper, when added to nickel to the extent of a few per cent, reduces the conductivity of the nickel.

The effect of various impurities on the conductivity of copper is shown in Fig. 195. If the copper for electrical conduction is to be strengthened and hardened by creating a solid solution in it of a second element, it is clear that the silicon offers distinct advantages over phosphorus. Cadmium up to 1 per cent is even

[1] STILLWELL, C. W., "Crystal Chemistry," p. 121, McGraw-Hill Book Company, Inc., New York, 1938.

better, as it raises the tensile strength nearly 100 per cent, with only 10 per cent loss in conductivity.   This alloy lasts three times as long as pure copper for trolley-wire service.   If high-resistance windings for an electric furnace or rheostat are to be designed, on the other hand, the more concentrated solid solutions are sought.

Intermetallic compounds have a conductivity that is always lower than the linear values calculated from the quantity of each constituent and its conductivity.   The lesser conductivity of
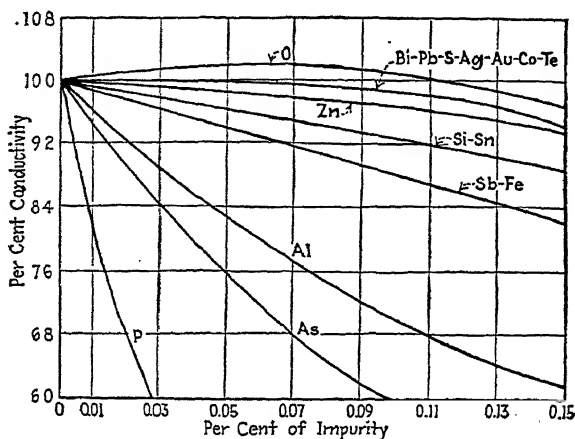
Fɪɢ. 195.—Effect of various "impurities" on the electrical conductivity of copper.
(*Czochralski, Z. Metallkunde,* **18,** 1, 1926.)

these compounds is to be expected from consideration of the greater tendency toward the formation of homopolar bonds in such instances and the thus greater restriction of the valence electrons.   If the compound forms solid solutions, its conductivity is further lowered according to the rule for solid solutions.

Conductivities of a Series of Alloys.—Combining these three types—solid solutions, duplex aggregates, and intermetallic compound—we have a diagram like Fig. 196 for the alloys of silver and magnesium.   From pure Ag, pure Mg, and pure MgAg, the curves drop rapidly for the solid solutions.   For aggregates of saturated solid solutions, the relation is a straight line, the conductivity depending on the amount of each crystal variety present. Thus, in general, if we know the conductivity of the saturated solid solution, points *B* and *C*, points *D* and *E,* and points *G* and

H, we can use the law of mixtures for any alloys between these points. The possibility of ever finding an alloy that conducts better than shown by the rule of mixtures for its components is thus denied. Figure 197 shows the very interesting diagram
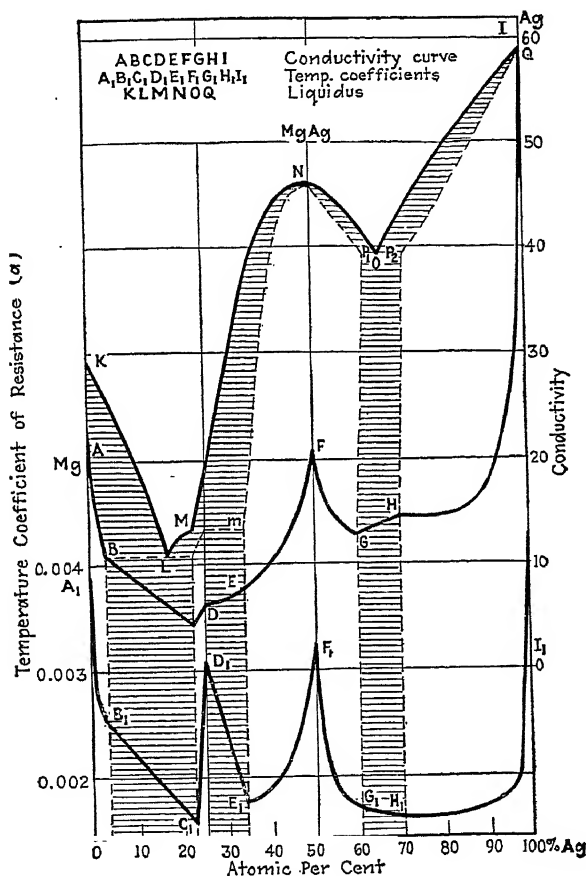
FIG. 196.—Electrical conductivities and temperature coefficients for alloys of magnesium-silver. (*Tammann.*)

for the *annealed* Au-Cu alloys. The *quenched* alloys of this system (or those tested at 500°C. as shown in Fig. 197) show a curve of exactly the same type as that of the Au-Ag alloys of Fig. 193, owing to supercooling (or decomposition) of the compounds AuCu and AuCu$_3$.

Heat Conductivity of Alloys.—The thermal conductivity changes in approximately the same way as was developed above for electrical conductivity. However, whereas in pure metals the heat conductivity was related to electrical conductivity by the Wiedemann-Franz ratio, in alloys the changes in heat conductivity with composition do not follow the changes in electrical conductivity according to this ratio, the changes
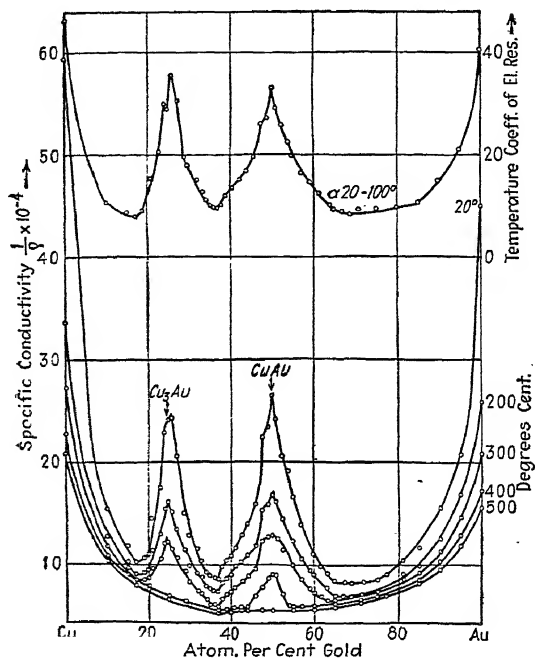
Fig. 197.—Conductivity isotherms and temperature coefficient of the annealed copper-gold alloys. (*Tammann.*)

being in the same direction but to a different degree. The same type catenary curve is obtained for solid solutions as was obtained for electrical conductivity. Such results are perhaps to be expected on the basis that even though heat conductivity is predominantly an electron function, a portion of its conductivity also arises from a direct collision of atoms. We would expect alloying to affect electron conductivity more than collision conductivity, with a result that, because electrical conductivity is entirely an electron function, the ratio between the two on alloying should not remain constant.

Recent investigations have shown that there is a definite relationship between the electrical and heat conductivity of alloys, although the Wiedemann-Franz ratio does not hold. If the thermal conductivity is plotted against the product of the electrical conductivity and the absolute temperature for any composition of alloy, a straight-line relationship results by means of which thermal conductivities can be calculated. The relationship for thermal conductivity is that

$$K \text{ (thermal conductivity)} = 5.02\lambda T \times 10^{-9} + 0.03,$$

where λ = electrical conductivity and T = absolute temperature.

As was pointed out for pure metals, thermal conductivity is an important property in engineering service, *e.g.*, the refrigeration industry, industrial and domestic heating, in heat interchangers and boilers, in internal combustion engines, in firearms, and in the heat-treatment of metal.

The Temperature Coefficient of Conductivity.—Both these conductivities change with changes of temperature, and for most metals the conductivity decreases with rise in temperature. Just as solid solutions show a low conductivity, so also they show a low-temperature coefficient of conductivity. The temperature coefficient for the alloys of silver and magnesium is also shown in Fig. 196. Alloys for potentiometers, bridges, galvanometers, and similar precision instruments should change their resistance as little as possible with changes in temperature. This service would also seek concentrated solid-solution alloys. Hence alloys, such as constantan (60 per cent copper, 40 per cent nickel) and manganin (84 per cent copper, 12 per cent nickel, and 4 per cent manganese), which have a temperature coefficient of practically zero in any ordinary range of temperature, are used. Their conductivity is about 0.05 that of copper. This invariability of resistivity is probably due to a nonequilibrium condition in the alloy, for after prolonged heating (for instance, by the electric current) the resistivity changes and becomes normal. Figure 197 shows the temperature coefficient of conductivity (and the conductivity isotherm) of the annealed Cu-Au alloys. The diagram illustrates the important effect of superlattice formation on properties.

Cold-working the alloys results in a small decrease in their electrical conductivity (see Chap. III). Chromium-nickel alloys are an exception to this rule.

High-resistance Alloys.[1]—The high-resistance alloys used extensively as electrical-resistance elements are quite definitely in the field of solid solutions. They are combinations, in general, of copper, nickel, and iron with one another or with further additions of chromium, manganese, or aluminum in amounts that do not exceed the solid-solution range.

Alloys that contain copper as the major constituent are limited, by reason of their easy oxidation, to operating temperatures not exceeding 300°C. The most commonly used are Constantan (55 copper and 45 nickel) with a low coefficient of electrical resistance, but a high-thermal e.m.f. against copper, and manganin (copper with manganese 10 to 12 and nickel 0–4) with a low coefficient of electrical resistance and a low-thermal e.m.f. against copper. The latter is used in standard resistances of high precision, the former for less precise resistances operating at low temperature.

Resistances for higher temperatures are based on nickel and iron. Nickel or iron alone is useful as ballast resistor up to the temperature of magnetic transformation, by reason of the high temperature coefficient of electrical resistance. But the important high resistors for high-temperature operation are essentially nickel 60 per cent, iron 20 per cent, chromium 15 to 20 per cent and nickel 80 per cent, chromium 20 per cent, the former having an operating range below 1000°C. and the latter capable of operating at 1100°C. and even higher for short intervals. Under various proprietary names—Nichrome, Chromel, Tophet, etc.—they are widely used in the field of industrial heating.

For operation at still higher temperatures, iron-chromium alloys with additions of aluminum to increase the electrical resistance are growing in favor. Because of their high melting point they are said to be capable of operating at temperatures around 1350°C.

A tabulation of the more important alloys with their electrical properties is shown in Table X.

[1] Courtesy of M. A. Hunter, Metallurgical Department, Rensselaer Polytechnic Institute, Troy, New York.

TABLE X.—HIGH-RESISTANCE ALLOYS

Alloys	Specific resistance at 20°C.		Temperature coefficient of resistance	
	Microhm cm.	Ohms per mil foot	T.C.	Range of temperature, degrees C.
Copper...............	1.72	10.37	0.00393	20
Nickel...............	10	60	0.0050	0–100
Iron.................	10	60	0.0050	0–100
Cu 55 Ni 45..........	49	294	±0.00002	20–100
Cu 88 Mn 12.........	48	290	±0.000015	15–35
Ni 70 Fe 30..........	20	120	0.0045	20–100
Ni 60 Fe 25 Cr 15.....	112	675	0.00017	20–100
Ni 80 Cr 20..........	108	650	0.00013	20–100
Fe 50 Ni 35 Cr 15.....	100	600	0.00031	20–500
Fe 80 Cr 15 Al 5......	167	1,000	−0.00035	20–500

[1] Courtesy of M. A. Hunter, Metallurgical Department, Rensselaer Polytechnic Institute, Troy, New York.

Magnetic Properties of Alloys.—The usefulness of various types of magnetic alloys depends upon the purposes for which they are to be utilized. Magnets may be classified generally as soft or temporary magnets and hard or permanent magnets.
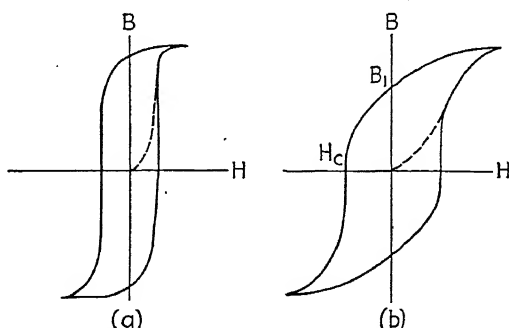
FIG. 198.—Hysteresis curves for hard and soft magnets.

The essential difference between the two is illustrated in Fig. 198. H is the intensity of the applied field in oersteds necessary to induce a field of B gausses (flux density) in a magnetic material. Upon removal of the field H, a certain residual magnetism B_r (remanance) is left in the piece, and a field H_c (coercive force) must be applied in the opposite direction to remove it. Another

term widely used in discussing magnetic material is permeability μ. Permeability is defined as the ratio between the induced magnetism B and the applied field H, $\mu = B/H$. A soft magnet is one in which a low field application induces a large field, and a slight coercive force is necessary to remove the remaining magnetism. The hysteresis loss is small for such materials, and the permeability is high. A hard magnet is one that is magnetized with difficulty, *i.e.*, a large applied field is necessary, μ is comparatively low, and H_c is high. With these facts in mind, we are prepared to examine the magnetism of alloys. The alloys of the three ferromagnetic metals, Fe, Co, and Ni, with
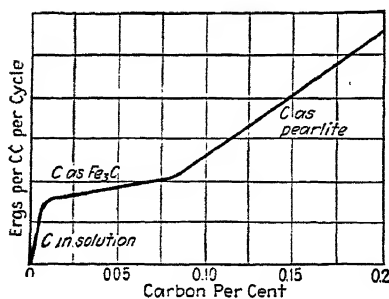
FIG. 199.—Effect of carbon on the hysteresis loss in iron. (*Smithells.*)

each other are all ferromagnetic, although the Fe-Ni alloys from 25 to 35 per cent Ni are only weakly so at room temperature. This is a region of retarded phase change. If the alloys in this region are made ferromagnetic by inducing the phase change by cooling below room temperature, they do not lose their magnetism until 600° upon reheating. They are known as irreversible magnetic alloys. Alloys of ferro- and nonferromagnetic elements show ferromagnetism over a part of the solid-solution range. The compounds FeO, Fe_3O_4, Fe_2O_3, FeS, also Fe_3P and Fe_2P, as well as Fe_3C, are ferromagnetic. Figure 199 shows the hysteresis loss of some Fe-C alloys. The rapid rise up to 0.005 per cent C is due to C in solid solution in α iron.

Soft magnets are desired for such purposes as electromagnets, transformer cores, and similar uses, where high permeability and low hysteresis losses are desirable. Large hysteresis losses in transformer cores, for example, would soon cause them to overheat and burn out. It has been found that elements that form interstitial solid solutions with Fe are those that broaden the hysteresis loop most markedly, so that for soft magnets such elements are undesirable and should be removed or replaced. Vacuum melting or hydrogen treatment to produce pure iron is sometimes employed, but such methods are expensive. Figure 200 shows the relative hysteresis losses in annealed and hydro-

genized iron. If, however, such elements as Si or Ni are added to the steel, which are substitutionally soluble in Fe, they reduce the interstitial solubility of such elements as C and thereby reduce the hysteresis. Such steels are used extensively as soft magnets.

The series Fe-Ni presents many interesting alloys. In the range 40 to 55 per cent Ni we have alloys characterized by high permeability at low field strength. These alloys make excellent soft magnets and are known as *permalloys*. Whereas the permeability of unannealed steel is 40 and electrolytic iron is 400
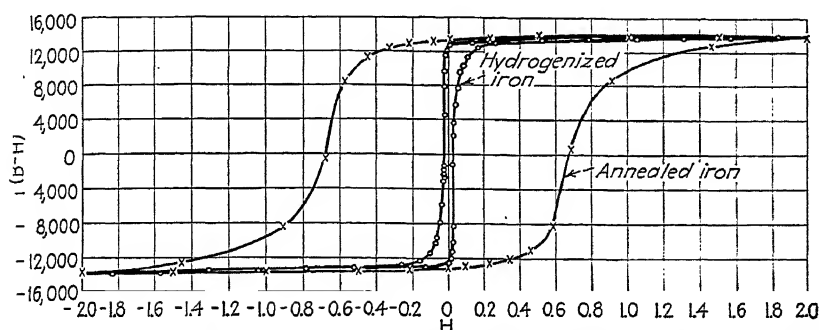
Fig. 200.—Relative hysteresis losses in annealed and hydrogenized iron. (*Cioffi, Phys. Rev.*, **39**, 364, 1932.)

to 800, the permeability of permalloy may be as high as 16,000. By special heat-treatment, the permeability of the alloy of 50 per cent Ni, called *Hypernik*, may be raised as high as 70,000. These alloys find much use as soft magnetic materials in telephone and radio transformers and relays. The alloys of 70 to 80 per cent Ni have extremely high permeabilities and are used, consequently, for such purposes as loading tape in submarine coils. Adequate theoretical explanation of these high permeabilities has not yet been developed. Figure 201 shows the large variation in permeabilities obtainable in the Fe-Ni-Co series.

The alloys of Fe-Co are interesting in that at certain compositions it is possible to obtain higher flux densities than in Fe itself.

In the Fe-Co-Ni ternary alloys we have an interesting series of alloys with practically constant permeabilities, known as *perminvars*. The constant permeability is attributed to a superlattice formation.

An interesting development in magnetic alloys is the heat-treatment of alloys in strong magnetic fields. By such treatment it has been possible to attain a permeability of 250,000 in 65 per cent Ni permalloy and 600,000 in hydrogen-treated iron, the explanation being that the alignment of magnetic
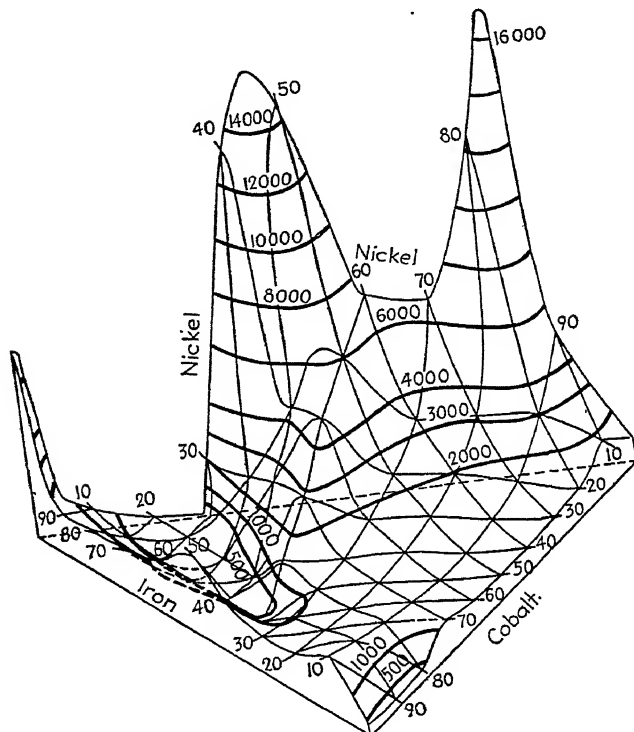
FIG. 201.—Variation of magnetic permeability in the Fe-Co-Ni system with composition. (*Bell System, July*, 1929.)

domains takes place at a temperature at which plastic flow of the metal is easy and no magnetostrictive strains are set up.

Hard, or permanent, magnets, on the other hand, are characterized by a low permeability, high coercive force, and a large hysteresis loop. The principle of the production of permanent magnets is to obtain, by alloying and proper heat-treatment, a finely divided precipitate throughout the matrix to key the structure and furnish resistance to change in magnetic condition, a property that is measured by coercive force. Alloys

of C, Mn, W, Mo, and Co are commonly used for the cheaper permanent magnets, in which the disperse phase is composed of finely divided carbides. Recently, more expensive alloys of Fe, Ni, and Al, or Fe, Co, and Mo have been developed that are of the precipitation hardening type, and extremely high coercive forces are obtainable. "Alnico," an Al-Ni-Co alloy, is of this type.

Surprising is the discovery of Heussler, who found that alloys of Mn with nonferromagnetic metals exhibit ferromagnetic properties. Here is a case where synthesis of two metals produces an alloy with a property almost totally lacking in its constituents. An alloy of 61 per cent Cu, 26 per cent Mn, and 13 per cent Al gives the best result. The magnetism is evidently associated with the compound Cu_2MnAl, as the magnetic intensity varies with the proportion of this phase present. By quenching these alloys from 800°C., a body-centered cubic lattice with a face-centered superlattice is obtained. The proper exchange forces for ferromagnetism evidently arise from the complicated lattice arrangement.

The Thermoelectric Force of Alloys.—The thermoelectric strength of alloys, since it depends to a great extent on the electrical and heat conductivity, varies generally with composition, as does the electrical and heat conductivity. If the conductivities of the pure metals of which a duplex series of alloys is composed are about the same, the thermoelectric force will vary as a straight line between them. Solid-solution series exhibit the same type catenary curve as electrical and thermal conductivities; however, there are a great many exceptions, the form of the curve varying in the opposite direction in some cases.

The utility of alloy couples depends upon the individual case. It is often possible to obtain much larger thermopotentials by the proper choice of alloy elements. The alloys of the poor conductors, Bi, Sb, Se, Te, exhibit exceptionally high thermopotentials, especially if an intermetallic compound, such as SeSn or Se_2Sn, is formed.

Bare metal thermocouples are used extensively in industrial control. Constantan (55Cu 45Ni) is used with copper or with iron for temperatures below 800°C. and chromel (90Ni 10Cr) with Alumel (Ni Al Si) up to 1000°C. For the higher ranges

up to 1500°C. a combination of platinum with a platinum-iridium or a platinum-rhodium alloy is required.

Figure 202 gives the e.m.f. of some standard metals and alloys against platinum from which the e.m.f. of any couple can be obtained.

Piezo Electricity.—Mention might also be made of the *piezo-electric* effect. If a crystal (*e.g.*, quartz) is compressed, a current
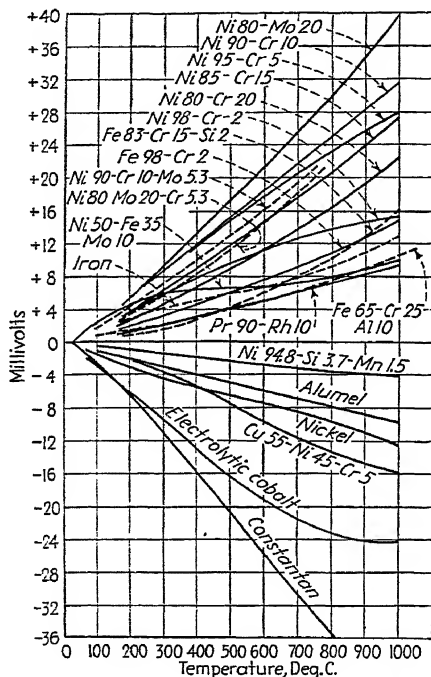
Fig. 202.—E.m.f. of standard metals and alloys against platinum.

flows through it and through a circuit connected with it. Conversely, if an alternating current is sent through such a crystal it will oscillate (expand and contract). The frequency of the current will determine the frequency of the oscillation.

The Chemical Properties of Duplex Alloys.—If an alloy consists of two varieties of crystallites, its stability or resistance to corrosion will in general be that of the least stable crystal present, or less.. The galvanic-cell action, which occurs when two unlike metals are joined and immersed in a conducting solution, is well known. Countless small local currents flow between the

two unlike metal grains of the alloy and back through the electro-
lyte or corrosive fluid, at the surface of the metal, thereby rapidly
dissolving the less "noble" or anodic grains.   Thus duplex alloys
(those containing two crystalline varieties) are usually very
rapidly corroded.   The slower corrosion of pure iron (ferrite)
as compared with steel (ferrite and cementite) is a familiar
example.   It seems, however, to be the Si, P, and S in the steel
that accelerate corrosion, as compared with electrolytic iron.
The carbide probably has a potential not much different from
that of iron (Tammann).   Striking is the corrosion rate of
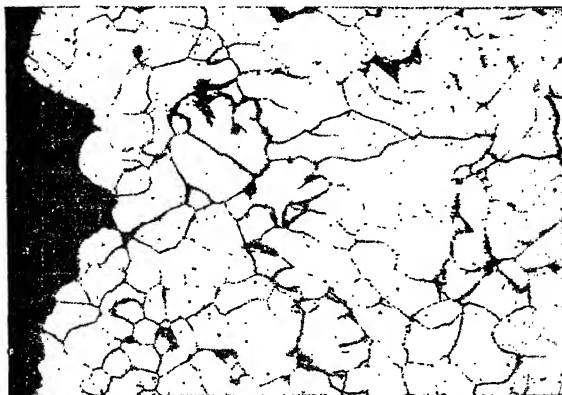
Fig. 203.—Grain-boundary corrosion of steel by alkaline solution ("caustic
embrittlement").   (*O. Schwarz.*)

chemically pure zinc, aluminum, and nickel, which is only a
fraction (for Zn 1/10,000) of that for the commercial metals.
If 0.001 per cent gold is added to zinc, the rate of solution in
0.5N hydrochloric acid is doubled.   *Intercrystalline corrosion* is
probably due to the presence of a second phase at the grain
boundaries.   The *caustic embrittlement* of boiler steel seems to
be due to alkalinity of the feed water and to intercrystalline
attack, as shown in Fig. 203.

Alloys of aluminum with silicon are duplex in structure but
have *increased* corrosion resistance as compared with pure
aluminum because, upon dissolving, the silicon forms a film of
$SiO_2 \cdot xH_2O$, which exerts a powerful protective action.[1]   An
addition of 0.02 per cent Al to Zn, or of Mg to Al, seems to
decrease the rate of solution.   Apparently the base-metal

[1] Köster and Müller, *Z. Metallkunde,* **19,** 52 (1927).

atoms form anodic spots, and the hydrogen liberated protects the principal metal.

The Chemical Properties of Solid Solutions.—If the additions form a solid solution with the original metal, the case is quite different. Here lies a possibility of *raising* the resistance to corrosion of the original metal by addition of a small amount of a second metal. Thus gold added to copper in jewelry improves its chemical stability. This stability is lost, however, for some alloys, if the temperature is raised much above the boiling point of water. The improvement in stability pro-
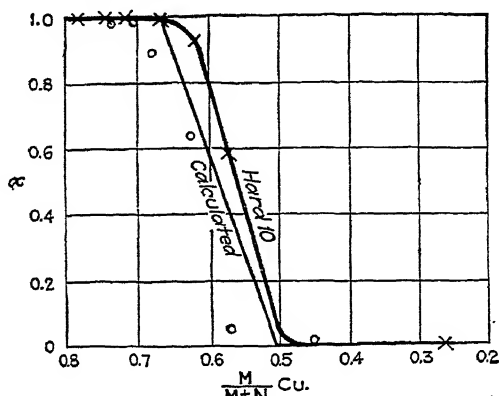
FIG. 204.—Fraction (α) of the soluble metal extracted from various gold-silver and copper-silver alloys by hot nitric acid. (*Tammann.*)

duced occurs at certain predetermined proportions of atoms of the added element and in fractions of $\frac{1}{8}$, $\frac{2}{8}$, $\frac{3}{8}$, etc.; *i.e.*, when $\frac{1}{8}$ of the atoms of the base metal are replaced by added metal atoms, a sudden improvement in stability may be looked for. If it does not appear at $\frac{1}{8}$, then it will not appear until the proportion is $\frac{2}{8}$ (25 atomic per cent), etc. In parting the alloys of gold with copper or silver from $\frac{8}{8}$ down to $\frac{4}{8}$ mol· gold, hot nitric acid will not produce any solution of metal, as shown in Fig. 204. From gold alloys of $\frac{4}{8}$ down to $\frac{3}{8}$ gold, the amount of extraction increases with decrease of gold content. In alloys below $\frac{3}{8}$ gold the soluble metal is completely extracted. Thus we see that, if $\frac{4}{8}$ gold or more is present, it protects the copper or silver completely from attack by nitric acid. The copper or silver has been "ennobled" by the addition of gold, which formed a solid solution with it. This case is exemplified by

the parting limits of gold-silver alloys in assaying. If gold is present above a certain amount, the metals cannot be parted even by boiling nitric acid. If they are remelted and more silver is added, they part readily in the acid.

This very useful behavior of solid solutions is explained by Tammann[1] in terms of the geometry of the space lattice of the solid solutions. He assumes (which recent X-ray studies deny) a uniform distribution of foreign and native atoms throughout the crystal lattice. The nobler atoms stand at one or more of the eight corners of the cube (in cubic lattices) and prevent the ingress of the attacking solvent ions as Cl, NO_3, for instance, thus protecting the base atoms from solution. A more recent theory, supported by X-ray analysis of the etched surfaces of gold-copper alloys, finds that the corrosion limit is due to the formation of a continuous layer of gold atoms (or ions) at the surface of the specimen, or to the absence of "coherent paths" of soluble atoms.[2] This behavior, however explained, gives us a means for using baser metals for corrosion resistance after first ennobling them by the addition of a small per-

FIG. 205.—The corrosion resistance of a series of alloys.

centage of a nobler and more costly metal. This principle is of very great importance industrially. The corrosion limits must be determined experimentally for each alloy series and for each corrosive solvent. At elevated temperatures the resistance limits disappear, owing to diffusion of the noble atoms out of their positions.

The corrosion resistance of a series of alloys is presented in Fig. 205. In the solid-solution region the resistance to corrosion remains constant, as is shown in this figure. As soon as a second phase appears, the corrosion resistance drops abruptly, owing to galvanic action. When the homogeneous solid solution on

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[1] TAMMANN, G., "Textbook of Metallography," p. 280, Chemical Publishing Company, Inc., New York, 1925.

[2] See MASING, *Trans. Am. Inst. Mining Met. Engrs.*, Institute of Metals Div., vol. 104, 1933.

the *B* side of the diagram is reached, the corrosion resistance suddenly becomes that of pure *B*.

As was noted in Chap. II, the early stages of corrosion at a metal surface may form a film of oxide, as in the case of aluminum, or of hydroxide, as in the case of magnesium; and this film is impervious to the further ingress of oxygen into the metal. These natural protective films play a very important part in corrosion resistance of certain metals and alloys. The presence of the film on aluminum may be demonstrated by heating electrically a fine aluminum wire suspended between supports. The wire melts but remains hanging, supported by the unmelted film. The addition of alloying elements may in some cases improve the tenacity of the film as, for example, the addition of Mn to Mg. The copper-bearing steels (0.2 to 1.0 per cent copper) resist atmospheric corrosion better than does ordinary steel, apparently owing to an invisible film of copper that forms over the steel surface.

The Stainless Steels.—Corrosion resistance may also be due to "passivity" of the metal surface. Iron, if dipped into concentrated nitric acid, loses the ability to precipitate silver or copper subsequently from sulphate solutions. It has become "passive," apparently owing to a layer or film of molecular oxygen on its surface. The catalytic action of metals, such as platinum sponge for instance, is usually attributed to a layer of gas adsorbed on the surface of the metal. The same condition of passivity may be produced on iron that is anodically polarized in a sulphuric acid solution. While this passive condition of iron is transient, that of alumino-thermically extracted chromium is retained. Both metals dissolve rapidly, however, in a warm hydrochloric acid solution. Both metals *lose* their passivity upon *cathodic* polarization in an acid electrolyte where nascent hydrogen is evolved. But, whereas iron after this latter treatment dissolves or oxidizes in a sulphuric acid solution or in nearly pure water, chromium does not, but *regains* passivity spontaneously. Tammann suspects that in the solid solutions of iron with chromium, as in the "stainless" steels, the chromium lends its passivity to the iron, when chromium is present in sufficient amount. This amount of chromium is determined by measuring the change in potential (electrochemical) of chromium-iron alloys after they have been cathodically polarized in a 0.05 mol H_2SO_4 solution.

It is found that steels with more than 15 per cent Cr become spontaneously less reactive (more passive), while those with 15 per cent or less do not. Anodic polarization of chromium steels renders them less reactive, but the effect is transient.

Tammann and Sotter[1] have measured the final potential of a number of chromium steels against the hydrogen electrode with the following results:

TABLE XI

Per cent Cr	After cathodic polarization	After anodic polarization
6	−0.25	−0.27
10	−0.29	−0.30
15	−0.27	−0.27
20	+0.55	+0.58
30	+0.62	+0.57
40	+0.61	+0.58

The steels with 15 per cent Cr or less are equally reactive after anodic and cathodic polarization; but those with 20 per cent Cr and more become spontaneously passive even after cathodic polarization.

Chromium steels can be divided into two classes of passivity in another way: The steels from 0 to 15 per cent Cr upon anodic polarization dissolve at 0.9 volt but are passive at voltages higher than this. Those from 20 to 40 per cent Cr transmit only a very small current through the cell even at voltages up to 2.1 volts. Whereas the former series of chromium steels is at first active and becomes passive above 0.9 volt only, the latter series is passive from the beginning and similar to a platinum electrode. Scratches on the surface diminish the passivity, probably on account of the potential differences between cold-worked and normal metal regions on the scratched surface (or to destruction of the film).

The idea that certain alloys containing Cr, Co, Ni, and Fe are "acid-proof" and suitable for substitution in place of platinum, means only that they are not attacked by concentrated nitric acid. In dilute acids, especially warm hydrochloric acid, or when oxygen access is limited, they dissolve, as do all "passive"

[1] *Z. anorg. Chemie*, **127**, 257, 1923.

metals.   Treatment with this (and other) acids or with hydrogen ions, removes the surface layer of oxygen upon which passivity depends.   Chromium forms this layer spontaneously, both in water and in air, while the more active iron rusts because the protecting layer of oxygen does not cling tightly to the surface.

The Corrosion of Alloys.—Corrosion is defined by Professor Guertler[1] as the gradual chemical attack of a metal under the influence of a moist atmosphere or of a natural or artificial solution.   Its importance in metallurgy is indicated by the use of paints, enamels, and porcelain on metal structures, by the growing use of rustless steels, by the widespread use of zinc, nickel, and chromium as coatings, and by the immense tonnage of metals scrapped each year as a result of the ravages of corrosion, where these and other preventives have not been applied or have not sufficed.

Simple atmospheric corrosion is of far greater importance than is the corrosion due to chemicals, for water and air are everywhere present.   Both air and liquid water are necessary for atmospheric corrosion, but even objects protected from rain will have liquid water condensed upon them by changes in temperature of the air carrying moisture.

Many theories of corrosion have been advanced, most of them concerned with iron and steel because of their extensive use and rapid corrosion.   The most widely held theory at present is as follows:

Iron, lying above hydrogen in the table of electrochemical potentials, can displace hydrogen atoms from H_2O.   It sends iron ions (Fe^{++}) into solution in water, displacing hydrogen ions (H^+) in H_2O.   Soon the layer of water surrounding the object will contain Fe^{++} and $2OH^-$ ions, *i.e.*, dissociated $Fe(OH)_2$, in considerable concentration.   If oxygen or air is admitted to this layer (by diffusion through the water), $Fe(OH)_3$ forms. This is less soluble than $Fe(OH)_2$ and precipitates as a brown deposit.   Since it forms not at the surface of the metal itself but in the adjacent solution, it does not cling tightly to the iron and does not protect it from further rusting, but scales off readily. It, or its later decomposition products, is called *rust*.

If a brightly polished piece of iron is corked up in a test tube full of boiled water, containing no air, rusting will not occur.

[1] *Metalltechnischer Kalendar*, 1926, p. 88.

If the cork is removed, the precipitate of $Fe(OH)_3$ forms rapidly. Both water and oxygen are necessary to corrosion of iron. Iron tanks, for instance, corrode faster if the water is flowing through them than if it is still. They corrode faster if they are filled and emptied, thus being exposed to air, than if they are kept full. Corrosion is more rapid when the air contains CO_2 and SO_2, which form acids in the water. In concentrated alkaline solutions iron readily becomes passive, apparently because iron does not take on a hydrogen charge

$$(Fe + 2HOH = Fe(OH)_2 + 2H^+),$$
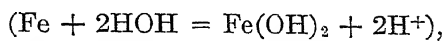
and because $Fe(OH)_2$ is less soluble in alkaline solution than it is in water.

Another factor, one of electrolytic nature, *differential aeration,* seems to play a part in the corrosion even of a pure metal. An iron sheet dipped into water with air above the water, corrodes only slightly at the region just below the water surface, but it corrodes rapidly deeper down in the water. Apparently the oxygen concentration is higher near the surface of the water and an electrolytic current flows between the two regions of different oxygen concentration. The region richer in oxygen is cathodic and does not dissolve rapidly, while the lower region is anodic in this "oxygen concentration cell" and dissolves rapidly.

In many practical instances one part of an object that is partly protected from access of oxygen will corrode more rapidly than an adjacent part that is exposed to a greater concentration of oxygen. For example, a pile of galvanized iron sheets showed more corrosion at the center of each sheet, where oxygen was partially excluded, than at the outer edges. The lower part of a city gas reservoir, where the metal was bathed with a gas that displaced oxygen from the water seal, corroded more than the parts exposed to a more oxidizing condition. A rubber ring on a corrosion-fatigue specimen caused failure to take place just under the rubber, where access of oxygen was severely restricted. A wood block pressed against a condenser tube diminished access of air to the tube at that point, and corrosion was most severe beneath the block. Tammann says, however, that, since this phenomenon has been observed also when oxygen is entirely absent, its interpretation in terms of an oxygen concentration cell is open to question.

Corrosion prevention is provided by coating the metal with paints, enamels, or other metals. Oxide films, such as those that form spontaneously on stainless steel, aluminum, and some other alloys, also offer protection. The metal coatings are mentioned on page 317.

Chemical coatings include *parkerizing,* or dipping into a bath of 2 per cent phosphoric acid, manganese dioxide, etc., and boiling to form a phosphate coating, after which the part is removed and dipped into oil. *Coslettizing* is similar. The *Barner-Barff* finish is produced by heating the part to 1600°F. and injecting superheated steam and CO_2 to form an oxide coating. The *Bontempi* finish is similar.

Properties of Quenched Alloys.—The rules given above for the estimation of the properties of a given alloy from a knowledge of the structure of the alloy will apply also when the structure is obtained by quenching. For instance, if a 13 per cent manganese steel is quenched so as to preserve homogeneous austenite, the alloy obviously will have the properties of a solid solution— *i.e.,* higher corrosion resistance, lower electrical conductivity, lower magnetic permeability, and higher strength and hardness than if it were cooled slowly and allowed to precipitate carbides.

Again, if a peritectic reaction is impeded by quenching and a duplex structure is obtained, the alloy will show the properties expected of a duplex structure. While these properties cannot be plotted under an equilibrium diagram as is done for alloys in the equilibrium states, it is clear that they can be derived from a knowledge of the microstructure of the alloy which remains after quenching, and these rules are, therefore, almost equally useful in estimating the properties of many heat-treated alloys.

Summary.—Summarizing briefly the relations between alloy structure and alloy properties, we see that the solid solutions show possibilities for improvements both in hardness and in corrosion-resistance qualities over the pure metals, but decided decrease in conductivity for both electricity and heat. Their formability remains high. Duplex alloys show average properties for hardness and conductivity between those of their constituents. Their resistance to corrosion is usually poor. The metallic compounds are outstanding for their very great hardness and brittleness. The magnetic properties show decided peaks at certain compositions. The coefficients of expansion show valleys

approaching zero at certain compositions. These generalizations, taken together with the idea of grouping the metals in families in the periodic table, make it possible to choose or modify an alloy for a given purpose with far greater assurance than it could be done by trial and error, as has been done for generations past.

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For additional literature references the reader should see end of Chap. IV.

Problem

1. For all the alloys of Fig. 132c, page 175, plot the probable hardness, electrical conductivity, density, and corrosion resistance at room temperature, assuming values for pure A, pure A_xB_y, and pure B.

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PART III
METAL TECHNOLOGY

CHAPTER IX

THE SHAPING OF METALS

In Parts I and II descriptions have been given of the behavior and properties of liquid and crystalline metals principally from the standpoint of natural science. Part III is devoted to the industrial aspects of physical metallurgy. In the present chapter the industrial shaping operations will be examined and described, and the practical application of the principles previously developed will be pointed out.

CASTING

Molds.—Most metallic objects begin their individual careers by being poured or "cast" while liquid into a fireproof container or "mold." If they are permitted to retain this shape in use or are reshaped by machining operations only, the objects are called *castings*. If they are to be subjected to subsequent deformation, such as rolling, forging, etc., the original shapes are called not castings but *ingots* or *blanks*. However, regardless of whether the objects are castings or ingots, the requirements for each are the same: good density and strength properties, and the least possible waste in pouring and subsequent operations.

FIG. 206.—Sand mold with core and gate. (*Geiger.*)

The mold may be of sand moistened with a "binder" such as molasses, and used in this moist condition, in which case it is called a *green sand mold,* or it may be baked to dry it and called a *dry sand mold.* To cast a hollow vessel, such as a pot, a "core" must be placed where the hollow is to be maintained, as shown in Fig. 206. A "gate" must be provided for pouring the metal into the mold, and "risers" to prevent entrapping gas and to insure that the metal will fill the mold at all parts. Openings,

called *vents,* are often provided for the escape of gas from the metal and the mold.

Instead of sand, a "permanent" or metal mold may be used where mass production of identical objects is desired—as in casting steel ingots in cast-iron molds (see Fig. 207), and in casting automobile pistons, and trim—instead of building up a new mold of sand each time.

Melting.—The metal so cast may come directly from the extraction of the ore as in the blast furnace (pig iron) with only one remelting, *i.e.,* in the cupola; from the open hearth (steel); from remelted copper cathodes; or from a Hall cell (aluminum). Or it may be remelted and alloyed, as in brass manufacture using copper and zinc. Loss of metal by evaporation and oxidation and a contamination of the melt by oxidation products are avoided by using a protective coating, such as charcoal; a molten salt or "flux," such as zinc chloride or ammonium chloride; or an "inactive" gas, such as nitrogen. Often, in spite of such precautions, a purification of the metal from oxygen is desirable before casting. This purification is called *deoxidation* and is exemplified by the poling of copper and the killing of steel.

Melting may also be done in the induction furnace, with improvement in control of quality of the metal.

Gas Absorption.—The solution of gases in the metal increases in general with rise in temperature and with the time of exposure at temperature. For this reason, casting is often done at the lowest temperature possible, and with the least delay. The increasing solubility of gases in liquid metals as the temperature rises is contrary to Henry's law. It is not an anomaly, however, but merely indicates that the solution of gases in metals is an endothermic process, whereas that of gases in aqueous liquids is exothermic[1] (van't Hoff's law: When the temperature of a system is raised, only that reaction can occur which is accompanied by an absorption of heat). On cooling in the mold, the dissolved gases are expelled from solution in the metal and escape slowly as bubbles.[2] If entrapped before escape from the metal is complete, these bubbles result in porosity. Such gases in the metal may come originally from the mold materials and from the

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[1] Scaff and Schumaker, *Metals & Alloys,* January, 1933, p. 8.

[2] Edwards, *J. Am. Inst. Mining Met. Engrs.,* 1935.

atmosphere. Porous molds may facilitate the escape of gases. The gases dissolved in molten aluminum can be removed by treatment with gaseous chlorine.[1] Subsequent treatment with BCl_3 gives a fine-grained casting.

Tough-pitch copper contains 0.04 per cent O_2 as Cu_2O at the grain boundaries. If poled below this oxygen content, it takes up gases from the furnace and gives unsound castings. If it is used at temperatures of 300° to 700°C. in contact with reducing gases (as H_2), the oxide at the grain boundaries is reduced, leaving the copper object in a brittle state.

Filling the Mold.—The liquid metal when cast must fill every part of the mold sharply before it solidifies, or a perfect casting will not be obtained. The fluidity of the liquid metal should, therefore, be high and the surface tension at the melting point low (see Liquid Metals, page 15). Castings may have blunt edges, owing to the presence of a film or skin of oxide on the metal, and

FIG. 207.—Metal molds for ingots. Bottom pouring. (*Moser.*)

not to the high surface tension of the liquid metal. The latent heat of fusion of the metal will influence the rate of solidification and therefore its ability to fill the mold before solidification, since heat is carried off by the mold at a limited rate only. Flow of liquid metal into the mold is not a simple straight-line flow but involves turbulent flow, which is not directly related to fluidity. Fluidity increases with rise in temperature, but so also does solubility for gases. Surface tension decreases slowly with rise in temperature. Thus vacuum melting would seem to permit higher casting temperatures, better fluidity, and surface-tension conditions without high gas content. The hydraulic pressure on the liquid metal tending to force it into all parts of the mold depends, of course, upon the density of the liquid metal and the height of the "head."

[1] ROSENHAIN, *J. Inst. Met.*, **44**, 305, 1931.

Molds may be top poured, as the sand mold shown in Fig. 206 on page 277, or bottom poured as in Fig. 207 above.   The latter method usually produces cleaner castings by floating out loose sand, slag, oxide skins on the surface, etc., instead of entrapping them.

Gas Evolution.—Upon solidification, the solubility of gases in metals usually decreases and the gases so rejected may either
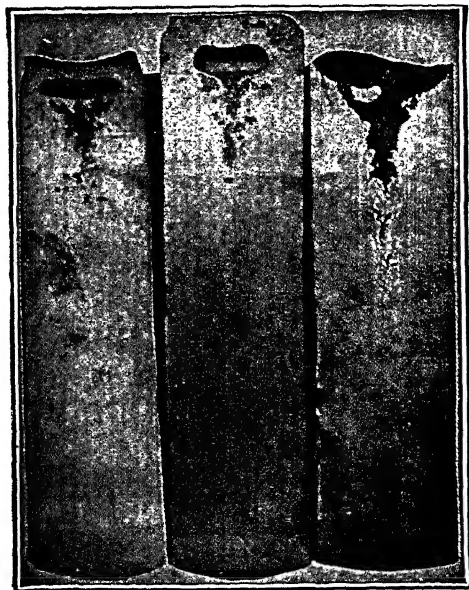
Fig. 208.—Pipes in steel ingots.   (*From Camps, " The Making, Shaping and Treating of Steel," Carnegie Steel Company.*)

rise as bubbles and escape, or may be entrapped in the solidifying metal.   In the important so-called *effervescing* steels it is evident that deoxidation or killing is incomplete, and the steel "froths" in the mold, accompanying the escape of CO and other gases. "Rimming" steel is one type of effervescing steel.   When the ingot is rolled, the gas cavities, if they were not at the surface, will have clean walls and will weld together.   When it is rolled into sheet, a low-carbon and exceptionally smooth surface is obtained.   The expansion of the metal due to separation of these bubbles reduces the volume of the pipe materially.   Segregation seems quite bad in these steels in many cases.   Gas cavities near the surface have oxidized walls and do not weld

together when the ingot is rolled. They cause "seams," which must be chipped out, or cut out with the oxyacetylene flame.

Pipe Formation.—If a mold is full of liquid metal it will not ordinarily be full after solidification, owing to the usual contraction of the metal in passing from the liquid to the crystalline state. This contraction in volume results in a *pipe* at the center and near the top of the usual steel ingot (see Fig. 208). The metal has solidified first at the bottom and side walls, and in a thin
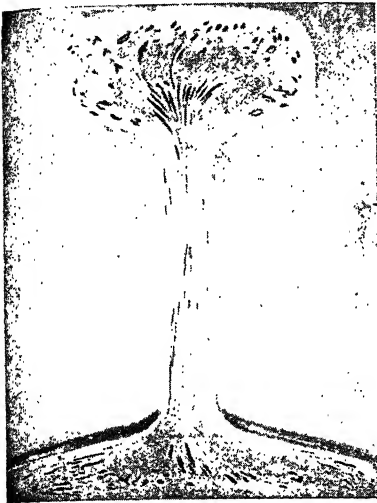
FIG. 209.—Rail section rolled from the top portion of a steel ingot. (*Oberhoffer.*)
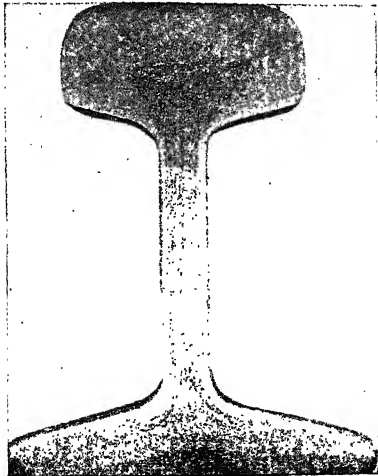
FIG. 210.—Same as Fig. 209 but from middle of ingot. (*Oberhoffer.*)

crust on top. The liquid remaining has fed the shrinkage of the other parts and is thus left with more volume than it can fill. Attempts to eliminate the pipe by keeping a reservoir of liquid metal above the ingot to supply the shrinkage ("hot-top ingots," "big-end-up") and by compressing the ingot before complete solidification ("fluid-compressed ingot") are effective but somewhat costly. The pipe, if rolled out with the ingot, will lengthen as the ingot lengthens. It is usually "cropped" off.

Segregation.—This last part of an ingot to solidify will contain the lowest melting liquid possible for the alloy, as shown by its equilibrium diagram. It will also contain much of the insoluble impurities, as slag particles, bits of sand and refractory, etc. (The discussion of insoluble impurities in castings given

on page 39 should be reread in this connection.)   This separa-. tion of first and last parts to solidify is called *ingot segregation*, as differentiated from *crystal segregation* or cored crystals, described under Alloys, page 162.   If rolled into a rod of circular section, a rectangular segregation zone will remain rectangular within the rod, as revealed by etching (see also Fig. 210).   Figure 209 shows the (unsound) etched cross section of a rail from the top of an ingot and Fig. 210 that from the middle of the ingot.

Shrinkage.   Inverse Segregation.—The crust of metal next to the mold walls continues to shrink after it has completed solidifi-
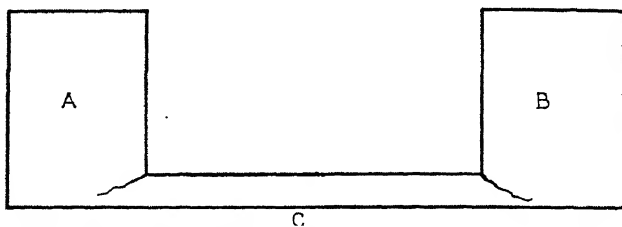
Fig. 211.- –Improper casting design.   Note abrupt change of section and sharp angles.

cation.   The outer dimensions of the object when it is cold are therefore less than would be anticipated.   The difference in dimensions is called *shrinkage*.   The pressure set up by this shrinkage may force metal that is still liquid from the center of the ingot out through the crust to the outside, where it appears as small beads.   This occurrence is called *inverse segregation* or *sweating*.   It is not at present fully understood.

Shrinkage Cracks.—The unequal cooling rates in different parts of the casting may result in internal stresses in the finished casting.   During cooling, while the metal is weak, these shrinkage stresses may actually tear the metal apart, causing internal "shrinkage cracks"—for example, where a thick section of metal joins a thin one.   Such cracks often require a redesign of the casting.   Figure 211 shows an improperly designed casting.   The long, thin section *C* cools rapidly and tears itself away from the heavy ends *A* and *B* which are still soft and held rigidly in the mold.   Owing to their larger mass, these parts *A* and *B* are passing through the pasty stage of weak resistance at the time the contraction of *C* takes place.   The casting should be redesigned and *C* be made heavier.   Shrinkage cracks are shown in Fig. 255,

page 338. Shrinkage stresses (not, of course, the cracks) are usually relieved by heating the finished casting to a temperature at which the metal is plastic.[1]

Rate of Cooling.—The rate of cooling of a casting determines, to a very large extent, what its properties will be. When liquid metal is poured into a cold metal mold, heat is lost rapidly by conduction to the mold, by radiation, and by convection to the surrounding air. Shrinkage of the ingot due to thermal contraction may remove it from contact with the mold walls, decreasing somewhat the rate of cooling.

Porosity is usually high in rapidly cooled castings. Both the dissolved gases, which are expelled from the metal when the temperature falls, and the gases entrapped by turbulence during pouring, have little opportunity to escape when the metal solidifies rapidly.

Ingot segregation of both soluble and insoluble impurities is low in rapidly cooled metal, though inverse segregation may be caused. Crystal segregation or coring is extensive. Internal stresses due to nonuniform cooling are high. On the other hand, if the conductivity of the mold be low, such as that of a sand mold, and if the mold itself be slowly cooled by the surrounding air only, the rate of solidification will be slow.

Very slow solidification would give opportunity for both dissolved and mechanically entrapped gases to escape, for the most part, on solidification. The material would be expected to be practically free of cooling stresses. Ingot segregation would be expected to be a maximum. Crystal segregation would be a minimum. Grains would be large and dendritic.

The physical properties of the castings would be commensurate with the above structures.

Die Casting.—If casting is done under pressure in a permanent mold, the effect of surface tension in rounding off sharp edges can be largely overcome and the amount of machining of the casting, as of screw threads, reduced. The *rate* of casting can also be accelerated in this machine operation. The process is called *pressure die casting*, the dimensions of the interior of the molds being so exact as to resemble a die. It is used in the mass production of small parts. Instead of being cast by means of

[1] See also MASING, G., A Few Problems in Non-ferrous Castings, *Metals & Alloys*, p. 99, July, 1933.

hydraulic pressure, the metal may be sucked into the mold by a vacuum. Zinc, lead, and aluminum alloys are commonly used. Automobile ornaments, cyclometer parts, valves, etc., are made in this way. Difficulty with the gradual swelling of the part in service, as in earlier zinc-base die castings, has been reduced.

Centrifugal Casting.—Cylindrical objects, such as pipes, may be cast by rotating a cylindrical permanent mold so rapidly that the liquid metal clings to the walls of the mold by centrifugal force, leaving the center hollow. The pouring spout *b* in Fig. 212
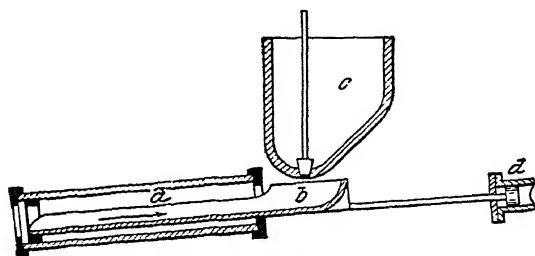
Fig. 212.—Centrifugal casting apparatus. (*Geiger.*)

is gradually moved along the inside of the mold by a piston. When withdrawn, the pipe is complete.

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POWDER METALLURGY

The powder method provides a means of fabricating highly refractory metals and metal compounds that cannot be cast by the usual melting process. In this process the powder particles are welded or sintered together, forming a continuous metal phase. Tungsten, molybdenum, and tantalum have melting points beyond the useful limit of any refractories now known; consequently, they must be obtained in the desired form at temperatures below their melting points. The powder method also provides a means of obtaining certain internal structures that cannot be secured by casting and subsequent hot working; specific examples are the production of thoriated tungsten filaments, oilless bearings, complex electrical contacts,

and cemented carbide tools. Since these alloys are not melted, the typical cast structures or segregations that develop during the freezing of a liquid are avoided. The field of powder metallurgy is relatively new and has only recently attained a position of commercial importance. However, its possibilities are now being realized and it is taking its place as an important metallurgical process.

Principles.—There are two general methods of manufacturing powder products. The proper powders are either pressed cold and subsequently heated, or they are pressed hot, the pressing and sintering taking place simultaneously. In the first case, any of the commercial heating processes may be utilized. In the hot-press method the compound is usually heated by its own electrical resistance.

The actual welding in the process is due to atomic surface forces, which are *not dependent on temperature*. High temperature acts merely to facilitate the contact obtainable and to increase the mobility of the atoms diffusing across the contact interface. The fact that high temperature is not necessary for welding is probably most strikingly illustrated in the case of glass. Surfaces of optically flat glass cleaned merely by the use of soap and water exhibit cohesive strength as high as 654 lb. per square inch when brought into intimate contact.

W. D. Jones illustrates the conditions governing cohesion between metal surfaces in a simple manner. Sheared surfaces of various metals (Pb, Sn, Zn, Cd, Cu, and Au) are prepared in such a way that a plane, highly polished cut face is obtained. It can then be shown that (1) the metals adhere strongly when pressed against themselves or each other; (2) the effect of adhesion is greater, the higher the temperature and the greater the plasticity of the metal, presumably because of the more complete contact obtainable; (3) a thin film of grease is sufficient to prevent all cohesion; and (4) a film of oxide thick enough to prevent cohesion may be dislodged by rubbing and abrading so that welding may be obtained.

The properties of the sintered object are dependent to a great extent upon the size and shape of the powder particles. Powders may be produced by various methods: milling, machining, shotting, granulation, atomizing, condensation of metallic vapors, reduction of oxide powders, chemical precipitation, or

electrolytic deposition. The density of the compact depends in part upon the ability of the powder to fill up voids by virtue of the proper range of particle size and shape. The strength of the compact depends upon the strength of the intergranular bonds, the extent of such bonded area, and the ability of the particles to key into one another. There is much controversy about the shape and size of particles that sinter best, and as a result particle characteristics are chosen on an empirical basis.

Pressure in the compacting process reduces porosity by forcing particles into voids, by deforming particles so that they key with one another, and by flattening out projections on the particle
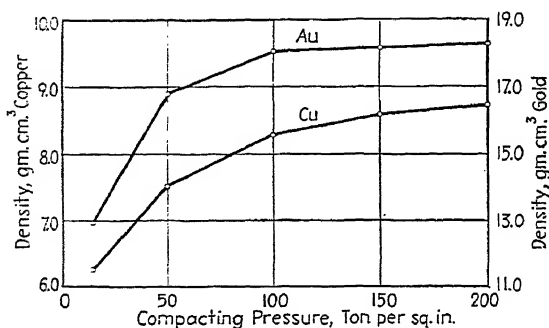
Fig. 213.—Density *vs.* compacting pressure in gold and copper powder compacts. (*Courtesy of Dr. W. D. Jones, "Powder Metallurgy," Edward Arnold and Company.*)

surfaces. The porosity decreases rapidly at first and then approaches a minimum asymptotically, as shown for Cu and Au in Fig. 213.

The effect of pressure on density is greatly dependent upon the method by which pressure is applied. Friction of the particles on the mold wall limits the depth to which a reasonably uniform pressure can be obtained. The use of tapered molds, multiple dies, or hydrostatic pressure partly eliminates the difficulty, but in many cases, for example in the manufacture of magnet cores where uniformity of physical characteristics is important, the depth of mold is limited to 0.5 cm. and high pressures are employed.

On heat-treating metal powder compacts, one of the first effects is the disturbance of the metal-gas-vapor equilibria. These disturbances may profoundly alter the final properties

of the compact. The gas may be either in solution or adsorbed on the surface. With increase in temperature, the gas may be either absorbed or evolved. Gas in a compact may exert its influence either by promoting porosity or by inhibiting adhesion. The potential sources of gas in a compressed powder are surface films of gas or vapor, mechanically trapped, and incidental or intentionally added volatile materials. The surface films or incidental volatile materials may be most effectively eliminated
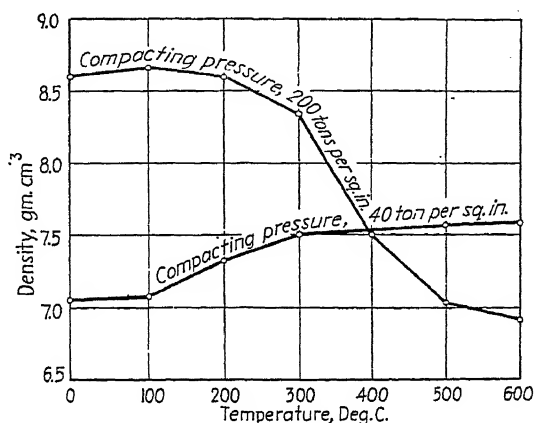
Fig. 214.—Density of copper compacts heated to various temperatures after compression under 40 tons per square inch and 200 tons per square inch. (*Courtesy of Dr. W. D. Jones, "Powder Metallurgy," Edward Arnold and Company.*)

in the preparation of the powder; however, mechanically trapped gases and the gases dissolved during compacting must be avoided by the proper choice of compacting pressure and heat-treatment. The more highly compacted the powder, the more tightly are the particles interlocked and the less opportunity is provided for the gas to escape. Thus, within limits, high pressures would be expected to yield higher porosities on heating if the compact has a high gas content. This effect is shown for cold-pressed Cu in Fig. 214.

Products.—The refractory powders are prepared by the reduction of the refractory oxides. These are then pressed cold with or without a binder. Subsequently the cold compact is given a preliminary sinter in a hydrogen or other protecting atmosphere, and finally in an atmosphere-controlled heat-treating furnace, using the high electrical resistance of the com-

pact for the internal generation of high temperatures. The microstructure of pure W is shown in Fig. 17, page 31.

The grain size and distribution of the constituents in the final product can be maintained practically the same as in the powder compact, and this is done in many important cases. Thus hard metallic carbides may be cemented in a strong matrix (usually cobalt, in which they are slightly soluble) to obtain the best structure for cutting tools. Electrical contact materials made by pressing successive layers of Cu and a Ag and graphite
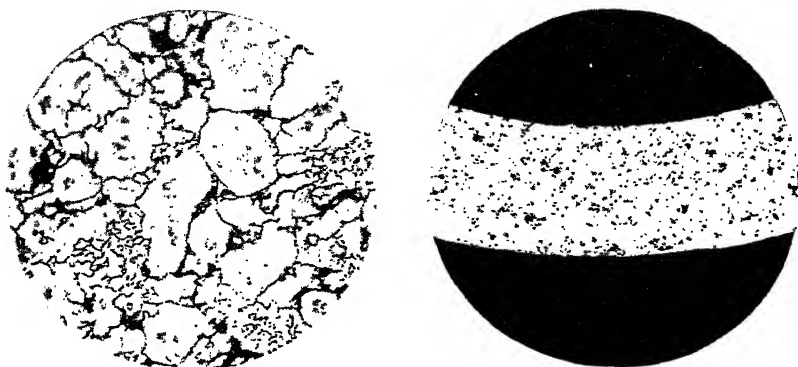
FIG. 215.—Micro- and macrostructures of porous bronze bearings. (*Courtesy of Dr. W. D. Jones, "Powder Metallurgy," Edward Arnold and Company.*)

mixture maintain the same distribution in the final state as in the powder state. Oilless bearings are produced by partial or incomplete sintering or by the introduction of volatile materials which, on sintering, form continuous pores of capillary size throughout the bearing. The bearings are then impregnated with oil, absorbing large quantities of the lubricant, and in use they continually supply the proper amount of lubricant to the shaft by capillary action. If the shaft heats up, the capillary flow of oil increases. Microstructures of porous bronze bearings are shown in Fig. 215.

The products just discussed represent those that can be produced by no other means except powder metallurgy. A general group of products that can be *more easily* produced by the powder method are materials that can be forged or cast only with difficulty, such as permanent magnets of Fe, Co, and Ni, high-purity products, articles that require excessive machining, bimetallic parts, etc.

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SHAPING IN THE SOLID STATE

Shaping Operations.—Subsequent to casting, further shaping operations are frequently desirable either to produce a new

Table XII.—Fiber Structure of Rolled Metals *(Sauerwald)*

Crystal lattice	Metal	Directions and planes parallel to direction of rolling		Frequency of the two positions
		Position I	Position II	
Cubic face-centered.	Cu, Ag	[112]‖WR(110)‖WE	....	For Al II scattered, I sharp, I:II = 1.4:1
	Al	[112]‖WR(110)‖WE	[111]‖WR(112)‖WE	II doubtful
	Pt	[112]‖WR(110)‖WE	[100]‖WR(001)‖WE	I predominant
	Au	[112]‖WR(110)‖WE	[100]‖WR(001)‖WE	
	α-Brass	[112]‖WR(110)‖WE		
Cubic body-centered.	α-Fe, Ta, W	[110]‖WR(100)‖WE		
Hexagonal...	Zn, Cd	[0001] 50° to 70° to perpendicular on plane of rolling	[100]‖WR	I faint (70 %) fibering II weak

WR = direction of rolling. *WE* = plane of rolling.

shape or to improve the properties of the metal. For the latter purpose, the piece should be reduced to at least two-fifths or one-fifth of its original size (see Chap. III). Shaping in the solid state is divided by the German writers into "chipping shape-giving," including the machining operations of sawing, and turning in a lathe; and "nonchipping shaping," such as forging, rolling, and pressing. The latter class will be considered first.

A table of methods of chipless shaping is given in Fig. 216. All these shaping operations involve deformation of the crystallites of which the metal is composed. The deformation of a *tension* specimen during testing of a zinc single crystal and of a
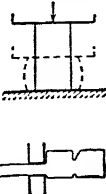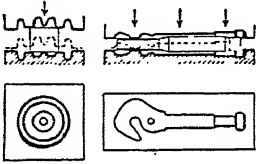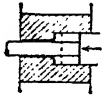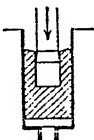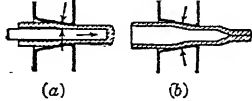
Method	Principle of operation	Action on metal
Forging Hammering Pressing		Pressure on unconfined metal
Die forging		Forces metal into a die
Extrusion		Squirts metal through a die
Piercing		Pressure exerted by mandrel on confined metal
Wire drawing		Wire or rod drawn through die
Tube drawing	(a) (b)	(a) Reduction in wall thickness between die and plug (b) "Sinking" or reduction in diameter

Fig. 216.—Survey of shaping operations.

polycrystalline body, both cold and hot, is described in Chap. III. The nature of the fiber structures resulting from *rolling* is given in Table XII. Those produced by other methods of deformation have scarcely been investigated. Much remains to be learned in this field. Figure 216 should be studied carefully.

Figure 217 shows from right to left the stages in conversion of a flat disk into a deep cup. Figures 218 and 219 show the *spinning* of an aluminum disk into a hollow vessel. The disk is rotated at high speed and forced against a chuck (whose form the blank is to take) by means of suitable tools, usually of wood in the case
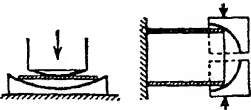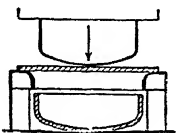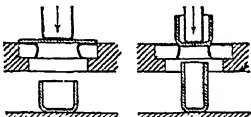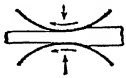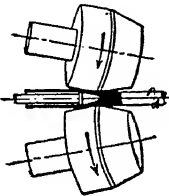
Method	Principle of operation	Action on metal
Stamping		(a) Curving plates (b) Curving ends of cylinder
Cupping Flanging Spinning		Bending edges of disk
Deep drawing		Stretching of walls (cartridge manufacture, automobile bodies)
Rolling of sheets, beams, and rails		Stretching by rolling
Piercing (Mannesmann)		Rolls and mandrel rotate in same direction

Fig. 216.—Survey of shaping operations. (*Continued.*)

of aluminum. The chuck rotates with the blank. The peripheral speeds are from 2,000 to 5,200 ft. per minute.

In the cold stamping of sheet, allowance must always be made for the "spring back," *i.e.*, the elastic part of the deformation, if accurate dimensions are desired.

The Flow of Metal in Shaping.—Macroscopically considered, without reference to crystallite orientation, one would expect a uniform flow of metal throughout the object being shaped. That this does not occur is shown in Fig. 220. The cylinder used

as a test specimen was split, and fine colored scratches were made on one of the cut surfaces. The halves are then joined and the cylinder was extruded through a die. The material at the center flows in advance of that at the sides. The influence of the angle of the die, roughness of the die, etc., has been investigated. In hammer forging, the surface layers are refined
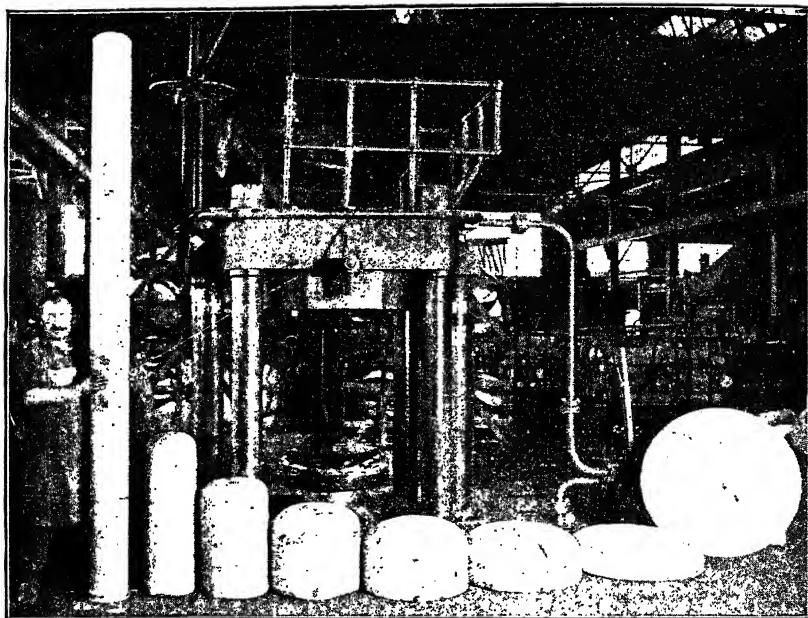
Fig. 217.—Stages in the conversion of a flat disk of aluminum into a deep cup. (*Edwards, Frary, and Jeffries, "The Aluminum Industry."*)

more than the interior metal. For this reason, pressed forgings are frequently preferred to hammer forgings. Figure 221 shows the flow of metal and slag stringers in the punching of wrought iron; Fig. 83, page 105, that of steel sheet.

Each of these shaping processes is important industrially and worthy of extended consideration. Furthermore, each feature of each process is important to the user of it: the energy consumed, the best temperature for shaping, the rate of shaping, the design of the machinery, the crystal structure and the properties of the finished object may each be of vital moment to the success of the operation. Each case is, however, merely an individual instance where the general principles for deforming and annealing,
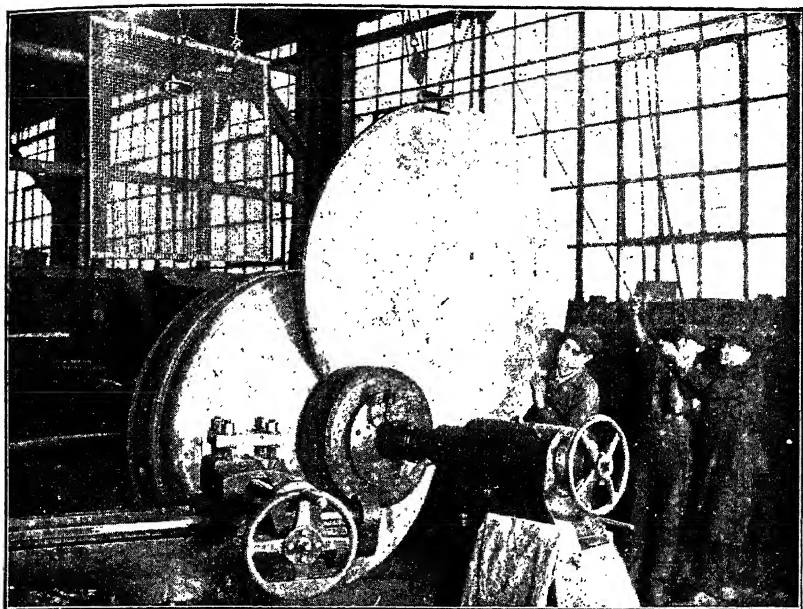
Fig. 218.—Inserting a 6-ft. aluminum disk into a spinning lathe.
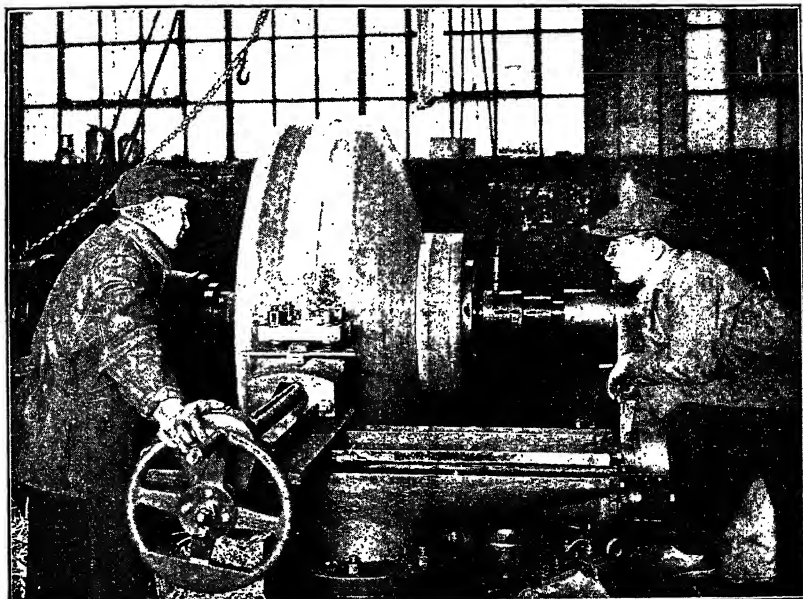
Fig. 219.—Spinning aluminum disk into a tank bottom. (*Edwards, Frary, and Jeffries, " The Aluminum Industry.*")

which we have developed in Chap. III, can be applied in solving the questions concerned in the special case.
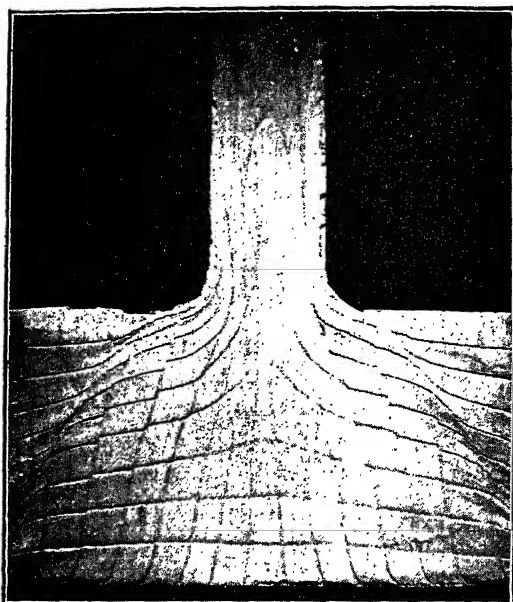
Fig. 220.—Flow of material in extrusion.   (*Riedel.*)
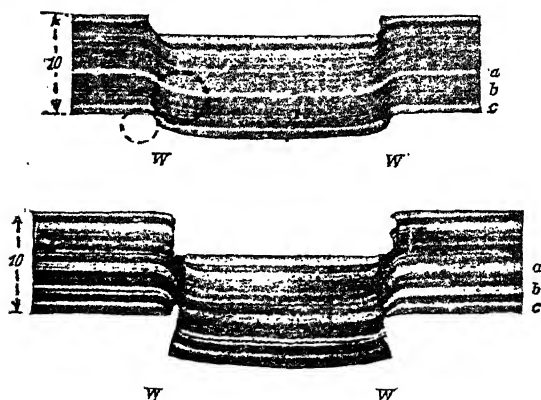
Fig. 221.—Flow of metal in punching wrought iron.   (*Czochralski.*)

Hot Shaping.—In some cases it will be desirable to shape the object while hot, in order to avoid fracture of the metal or of the shaping machinery, and to consume less power and less time in the operation.   Cold shaping, on the other hand, gives an

unoxidized surface, greater accuracy of dimensions, and an increase in hardness and strength of the metal. After several cold-shaping operations, an annealing is usually necessary to soften the metal before shaping is continued.

Figure 222 shows[1] the grain size of soft steel after hot-working to varying degrees at various temperatures. The specimens were held from 5 to 30 min. at temperature, subsequent to working, and then cooled. At 600°C. there was no change in the grain size, but at 750°C., with a deformation of 6 per cent, the grain size was 50 times that before working began.
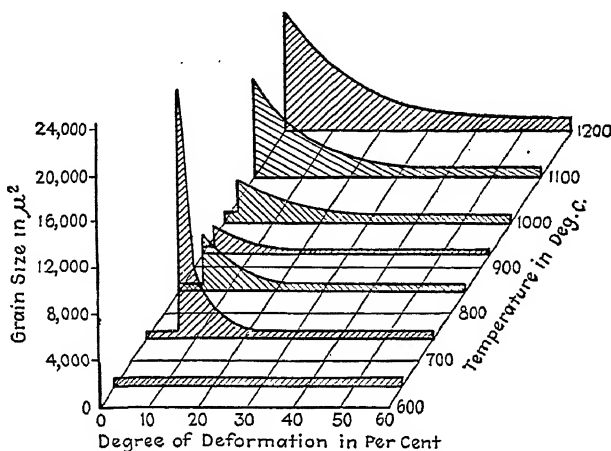
FIG. 222.—Grain size of soft steel after working to various extents at various temperatures.

Since a coarse grain size injures the mechanical properties, Hanemann calls this the *dangerous temperature range*. At higher temperatures this condition occurs at lower degrees of deformation, as the graph shows (see also Finishing Temperature, page 119).

In copper at 900°C. and 1.2 per cent deformation, the grain size is 10,000 times that with 20 per cent deformation (Tammann).

Table XIII gives the shaping and annealing temperatures for a number of metals and alloys.

Rolling.—Because of the fact that most of the final shaping operations utilize rolled products—*e.g.*, sheet, strip, plate, rods, bars—as their raw materials, and because an important tonnage

[1] HANEMANN and SCHNEIDER, *Stahl u. Eisen*, **49**, 7, 1929.

TABLE XIII.—TEMPERATURES OF MECHANICAL TREATMENT OF SOME METALS AND ALLOYS (Stoughton and Butts)

Metal	Can it be worked cold?	Best temperatures for working, degrees centigrade	Best finishing temperature, degrees centigrade	Softening temperature degrees centigrade,***,†† for ½ hr.	Temperatures of non-malleability, degrees centigrade	Recrystallizing temperature, degrees centigrade (minimum)
Aluminum	Yes*	450 to 425§	....	150 to 350	550 up	150
Antimony	No	....	....	None	All	Melting
Bismuth	No	....	....	None	All	Melting
Brass	Yes	Usually cold	....	250 to 500	600 up	250 to 500
Bronze	Yes	Usually cold	....	....	....	500
Cobalt	No	500 to 600	....	None	All	Melting
Copper	Easily*	800 to 750	....	400 to 700	800 up	200
Duralumin	Yes†	450 to 350	Cold†	530	†	530
Iron and soft steel	Yes*	1100 to 900	900	100 to 930	350 to 900	450
Lead	Very easily	Cold	Cold	....	None	20§§
Magnesium	No	500 to 300§,||	380	....	420 up	Melting
Molybdenum	No‡	....	....	....	....	Melting
Monel metal	Yes	1150 to 900	900	850 to 1000	540 to 870	930
Nickel	Yes	1200 to 1100	900	700 to 900	540 to 870	700
18 Cr, 8 Ni stainless steel	Yes	1250 to 950	....	900	....	....
Steel—structural	Slightly	1100 to 900	900	850 to 900	350 to 900	600
Steel—high-carbon	No	1100 to 700	700	250 to 700	350 to 700	700
Stellite	No	....	....	Cannot be softened	All‡	....
Tin	Very easily	Cold	Cold	100 to 150	200	20
Tungsten	No‡	1600 to 600	600	....	Cold	1200
Zinc	No	150 to 110	110 to 150	60 to 150	260	20

* Large pieces rolled hot, then finished cold.
† After heat treatment, duralumin can be worked cold for about 45 min.
‡ Ductile at atmospheric temperature, but not malleable.
§ Rods and other appropriate shapes are extruded in preference to rolling.
|| Must be exactly within this range.
¶ The softer varieties.
** Prolongation of the annealing time is equivalent to a slightly higher temperature.
†† With less than 5 per cent deformation, the temperature of complete softening is higher and coarse grain size results in most materials;
‡‡ The harder varieties.
§§ Storing at room temperature produces coarse grain size.

of rolled structural shapes is used in this state, the rolling process merits further consideration. The purpose of rolling is to convert large sections (usually ingots) to one of the various shapes mentioned above. The required change in shape is accomplished by the use of compression between rolls for the purpose of producing elongation. Accompanying the process is also an unavoidable but small amount of lateral spreading at right angles to the elongation. The amount and the importance of the spreading depend primarily upon the size of the ingot, the roll design, the amount of reduction, pressure, temperature, and the roll surface. In some cases of rolling specific sizes and shapes (rails, beams, etc.), often called *die rolling*, it is necessary to restrict lateral spreading to required limits, with
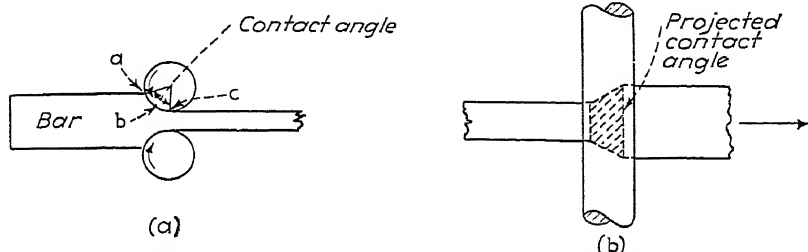
Fig. 223.—Diagrammatic illustration of the rolling process.

a result that the stress analysis in die rolling becomes a very difficult problem.

Figure 223 illustrates the contact angle and contact area in the plain rolling of a bar. In the rolling of a bar, the cross-sectional area emerging from the rolls is less and the length is greater than that entering them. Therefore the bar must leave the rolls at a faster speed than it entered. As shown in Fig. 223a the speed of the bar from point a to point b is usually less than the peripheral roll speed, at point b the speed of the bar equals that of the roll surface, and from point b to point c the speed of the bar exceeds that of the rolls. It follows, then, that with a constant speed of the rolls, there must be slippage or relative motion between the rolls and the bar. This slippage accounts for roll wear and results in an "extrusion effect" or "forward slip" encountered in rolling.

The economy of rolling depends upon the amount of reduction that can be made in a single roll pass. The fewer the passes

required, the less the cost and time required to finish the shape. The limitations placed upon the amount of reduction per pass are as follows. (1) The size of the material offered to the rolls relative to the size of the rolls determines whether or not the material will enter between the rolls. The "bite" of the rolls depends upon the contact angle (Fig. 223a) and the surface conditions of the rolls and the material being rolled (friction, lubrication, pressure, design, etc.). If the reduction is too great, the grip of the rolls will be insufficient and the bar will not enter. (2) The strength of the rolls themselves greatly limits reduction, in that the greater the reduction, the greater the contact areas (Fig. 223b) and consequently the greater the stress on the rolls. Besides the pure tension and compression stresses set up in the rolls by simple bending, the rotation of the rolls alternates those stresses on the surface and the roll is subject to fatigue. As discussed in Chap. III, surface imperfections serve to concentrate stress in fatigue, and consequently the surface condition of the rolls becomes important. (3) Great reductions require much power, and the capacity of the motors driving the rolls is sometimes the limiting factor. (4) The greater the reduction, the greater the difference in entering and leaving speed of the bar, and the greater the relative slip or extrusion effect. The roll wear consequently increases with reduction and is sometimes the limiting factor. (5) The formability of the bar itself is the most important limiting factor. All the factors of work hardening, preferred orientation, and the consequent deformation limits, and the effect of temperature on the relief of work hardening, as was discussed in Chap. III, come into play in determining the limits of reduction per pass.

The Machining of Metals.—In this operation a sharp, hard edge, such as the point of a lathe tool, or a saw tooth, deforms the metal, as shown, for example, in Fig. 224. Similar deformation occurs in drilling, milling, grinding, wearing, etc. The chips may be long, torn shavings as produced in Fig. 224, or clean, short chips as in Fig. 225.

The temperature at the tip of the tool rises rapidly during machining. The rise can be nicely measured by a thermocouple consisting of the tool as one element and the object machined as the other element of the thermocouple. The temperature reached 600°C. in some cases, and the tool must,

therefore, be "self-hardening" or it will lose its "edge."
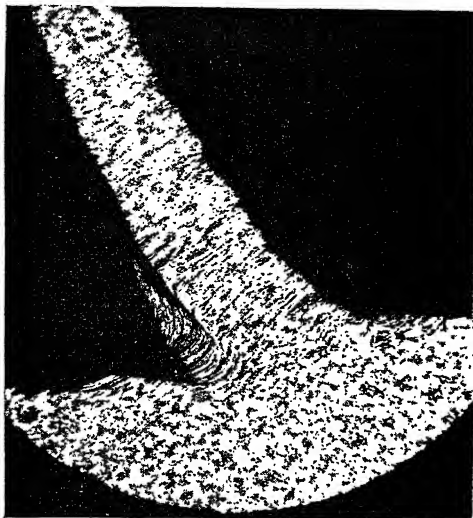
FIG. 224.—Deformation of a metal "shaving" produced by a lathe tool. (*Courtesy of Hans Ernst and The Cincinnati Milling Machine Company.*)

FIG. 225.—Machining a more brittle metal. (*Courtesy of Hans Ernst and The Cincinnati Milling Machine Company.*)

Machinability[1] is an important property of a metal used in manufacturing operations. It is measured as the quantity of chips that can be removed in a given time, as the weight of chips

[1] See BOSTON, O. W., *Trans. Am. Soc. Mech. Engrs.*, **48**, 705, 1926.

or "turnings" per hour. Since the behavior of the tool is important also, one may choose to determine machinability in terms of the useful life of the tool used, or in terms of the energy absorbed in machining 1 lb. of chips or turnings.

Taylor measured the cutting qualities of a tool by measuring the fastest speed of turning that permitted the tool to hold its edge for 20 min.

The relation between internal structure, hardness, and tensile strength of the metallic object and its machinability has not been established. The cutting action of knives has scarcely been investigated, until recently by Honda in Japan.

WELDING AND CUTTING METALS

The Metallurgy of Welding Processes.—Welding, brazing, and soldering are processes in which parts are joined by means of the forces of interatomic attraction acting across the joint. Riveting, bolting, and other mechanical methods of joining parts do not depend upon atomic forces to act across the joint, but simply upon the rigidity of the parts and of the connectors. Thus a riveted joint may connect two steel surfaces, each surface being coated with scale or rust, so that there is no intimate contact across the joint and no atomic attraction between the contact surfaces. Welds, on the contrary, require clean, intimate contact at the joint, so that the atoms in opposite faces come close enough to attract each other and bind or weld the parts.

In fact, clean and intimate contact alone, without any heating or hammering, may be sufficient to produce a weld. When metal surfaces are machined quite truly plane, and ground and polished and simply brought into contact without any pressure, it has been found that they will cling so tightly that forcible separation tears bits of metal out of the opposite contact faces. Such surfaces are extremely difficult to produce, but the experiment is illuminating.

Pressure Welding.—Such clean and intimate contact is more readily produced if the parts are heated to the plastic state and hammered so as to conform intimately to each other at the contact. Thus the blacksmith worked, adding a bit of borax as flux to melt and dissolve away the scale of oxides to form a fluid glass, which his hammer blows squeezed out, leaving clean

metal in intimate contact across the junction. His forge fire was irregular and slow. The parts to be joined are now heated electrically, instead, and are pressed into contact while plastic instead of being hammered. The current flows through the parts to be joined and heats them, but heats them most rapidly *at the contact* between the parts, where the electrical resistance is highest, exactly where the heat is wanted. When the parts are plastic at the joint, pressure is applied which squeezes out the scale and oxide. This method is called *electrical resistance welding*. When the electrical power applied is very great and the period of application is short, it is called *flash welding*. Other modifications are called *spot welding, percussion welding, projection welding, seam welding*, and *shot welding*. These methods are used in the most varied ways; for instance, to form pipe out of sheet by rolling the sheet into a cylinder and welding the longitudinal seam; to weld 60-in.-long edges of a sheet $\frac{1}{8}$ in. thick in automobile-body construction, and to fabricate lamp shades, metal chairs, and lockers, refrigerator machinery, and countless similar objects. All the above methods require the application of pressure while the metal is hot and are called *pressure-welding* processes.

Fusion Welding.—Clean and intimate contact between the parts to be joined, or between them and an intermediate body, such as solder, may also be obtained by *fusion* of the parts or of the solder, or of both. Such processes are called *fusion welding, soldering*, and *brazing*. The heat may be supplied by a chemical reaction, as in the oxyacetylene process

$$(C_2H_2 + 2\tfrac{1}{2}O_2 = 2CO_2 + H_2O + \text{heat})$$
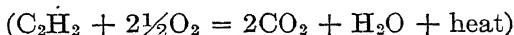
the thermit process

$$(2Al + Fe_2O_3 = Al_2O_3 + 2Fe + \text{heat})$$
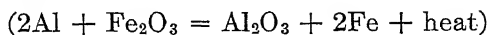
the blow torch for soldering, the gas furnace in copper brazing, or by the electric arc discharge in electric arc welding. In all cases of fusion, union of liquid metal is produced and union with the parts takes place in the liquid state. Solidification of the metal leaves an intimate junction. The junction must be clean, of course, and may be cleaned previously by chemical or mechanical means (grinding, etching with acid, etc.). Some cleansing is

usually accomplished by the floating out of impurities melted at the surfaces to be joined.

The Structures and Properties of Welds.—While each one of the above-mentioned processes has a host of interesting scientific features and practical applications, they cannot be discussed in this book. Some aspects fall into a general class, however, and are worthy of examination. For instance, the quality of the metal in the joint and the effect of heating upon the metal adjacent to the joint are important metallurgically.

In the pressure-welding processes, the metal in the joint is heated to the plastic condition, or above, and compressed while hot. The effect is a hot-working treatment as described on page 128, resulting in some grain refinement. All the principles of finishing temperature, internal stresses, recrystallization, grain growth, and physical properties, discussed previously in the general case, apply in these cases also. The union is essentially a "forging."

In fusion welding, the connection metal, whether melted from the edges to be joined (*autogenous welding*), or supplied separately, solidifies from the liquid state and usually cools below the recrystallization temperature without any applied deformation. Fusion welds are, therefore, essentially castings. Since the surrounding parts are of good conductors of heat, the fusion weld may be called a *chilled casting*, and its structure will, therefore, usually be columnar. Subsequent operations on the fusion weld, such as hammering and annealing, may, of course, be carried out to modify the cast structures beneficially, as is actually the case, for instance, in boiler manufacture by welding. As in other casting operations, the action of the atmosphere on the melted metal,[1] its fluidity and surface tension, the solidification process,[2] including segregation and shrinkage, all play their anticipated important rôles, as described at the beginning of this chapter, but the effect may appear different in each variety of the operation. The stresses set up in the weld by shrinkage are often of considerable importance. These stresses may be relieved by annealing the entire object after welding is finished. The usual practice is to hold it at about 600°C. one hour for each inch of thickness of the object.

[1] N, G. E., *Metal Progress*, January, February, 1932.
[2] DOAN, G. E., *Am. Welding Soc. J.*, 1932.

The Structure and Properties of the Zone beneath the Weld.—
The effect of the welding heat upon the metal immediately
adjacent to the weld is likewise important and dependent upon
the chemical composition and previous shaping treatment that the
metal has received. The temperature gradient from the weld
into the adjacent metal is very sharp, and sharper in fusion weld-
ing than in forge or electrical resistance welding, or in brazing
and soldering, since these other processes do not require a melting
of the parts (brazing and soldering employ a joining metal that
is lower in melting point than the parts joined). In fusion weld-
ing the surfaces of the parts are at their melting point, or above,
and in some cases the temperature grades rapidly through all
intermediate temperatures and within a fraction of an inch
from the weld reaches room temperature. In the successive
regions of this heated zone, we may then expect to find the metal
cooled rapidly from every intermediate temperature between
room temperature and the metal's melting point. For, since
metals are good conductors of heat, the passage of the welding
operation past a given point leaves this heated zone to suffer
a rapid cooling by conduction of heat into the surrounding regions
of the metal, in other words, a quenching effect (see page 313,
Quenching) tending to retain in this zone the conditions created
there by the high temperature. Thus grain growth may occur
near the weld, or recrystallization if the parts were cold-worked
prior to welding, or in alloy steels, austenite may have been
produced and only partly decomposed during cooling, or in
cast iron a white-iron region may result, just as if each of these
metals had been heated to a high temperature and cooled rapidly.
The results for any given alloy will follow the equilibrium
diagram of the alloy, with account taken of the rapidity of cooling
and the laws of recrystallization and grain growth. The metal-
lurgy of welding requires a consideration of the chemical and
physical effects incidental to the process, as well as to the thermal
changes in the weld region.

A survey of the arc-welding process, for example, will show
that it involves almost every principle of metallurgy covered
in this text.

1. When the welding rod and base metal are melted, all the
phenomena of gas absorption, surface tension, viscosity, and gas
escape come into play, just as they do in steel foundry practice.

The surface tension may be lowered by adding less than 1 per cent antimony to the coating, causing a spreading effect on the liquid metal and speeding up the melting operation.

2. The atmosphere acts on the superheated, finely divided metal just as it does in the bessemer converter, burning out carbon and silicon and tending to remain dissolved in the iron. The shielded arc partially prevents these actions.

3. A cast structure is formed by the freezing of the weld, one with the columnar structure of an ingot, owing to the rapid chill, and with piping and segregation.

4. The "casting" fastened to the sides of the "mold" shrinks, setting up high internal stresses and deforming or sometimes cracking the metal.

5. Any previous heat-treatment or cold working of the base metal is partially or completely destroyed by the heat flowing out of the weld.

6. The rapid cooling of the weld zone by conduction (and radiation) from above the critical temperature results in the decomposition of austenite at subcritical temperatures, involving thus the entire "S-curve" phenomena.

7. The weld, containing oxygen and nitrogen compounds in supersaturated solution, now age-hardens, to a lesser degree in coated electrode welds than in bare wire welds, rising in tensile strength and losing ductility.

8. Testing, both destructive and nondestructive, is an important step.

Some Modern Uses of the Welding Processes.—The industrial importance of these joining operations in giving shape to metal objects is rapidly increasing. The steel framework for a 14-story building has been erected entirely by fusion welding, thus eliminating the noise of riveting and the loss of strength where rivet holes are punched, and saving some weight in steel. This building framework is shown in Fig. 226. Pipe lines from oil fields, battleships, boilers, and bridges are now formed by this process. In the mass production of identical parts, as in the automobile, refrigerator, radio, electric motor, piping, and other industries, the pressure-welding methods are producing enormous savings and the extent of their use is rapidly increasing. Welded objects built up of simple parts of sheet, rods, and angle iron are replacing complicated and expensive castings,

in many cases, as shown for a Diesel engine crankcase assembly in Fig. 227.
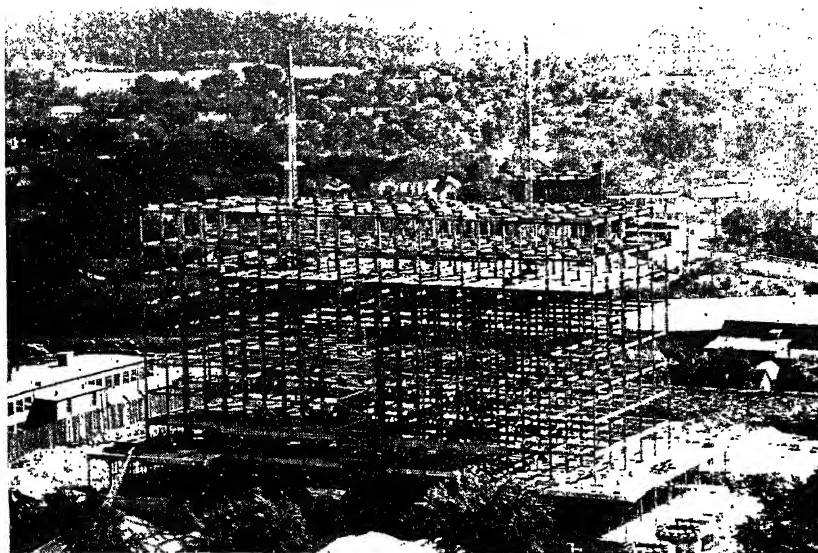
FIG. 226.—All-welded framework of a 14-story building. (*Courtesy of Lincoln Electric Company.*)
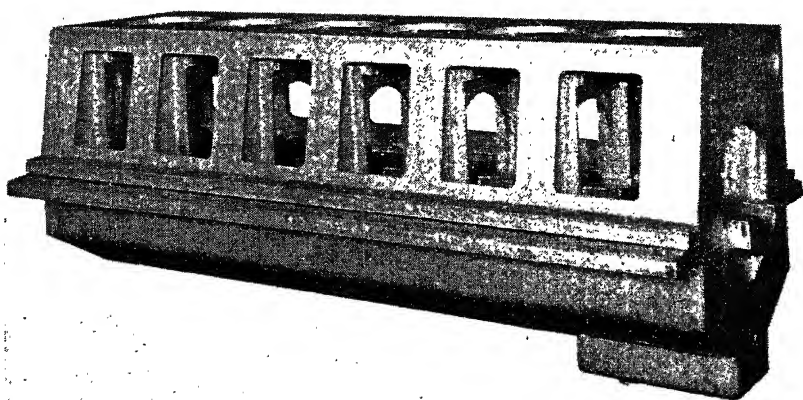
FIG. 227.—Welded Diesel engine crankcase assembly. (*Courtesy of Lukenweld, Inc.*)

The cutting of metals may be accomplished by the machining operations mentioned previously, but certain chemical methods

employing oxygen are of great importance.   The oxyacetylene process and the oxygen lance operate by *burning* a narrow slot through the metal, which has been previously heated at one point to its ignition temperature.   The heat evolved by oxidation of the metal is sufficient to maintain it above its ignition temperature, and the pressure of the gas stream drives the oxidized metal out of the slot.   While the method sounds crude and ineffective, it is surprisingly powerful and accurate.   A cut about $\frac{1}{2}$ in.
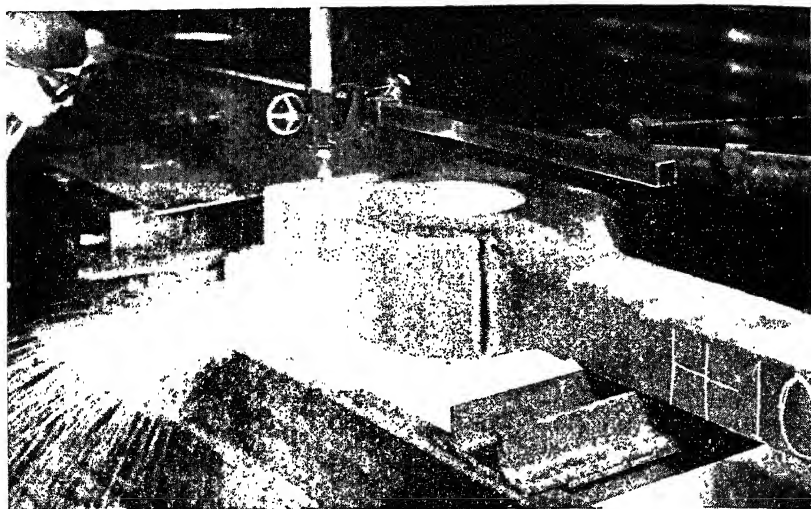
Fig. 228.—Trimming the outside of a locomotive main driving rod.   Back end.
(*Courtesy of Linde Company.*)

wide and perfectly true may be cut through steel more than a foot thick, by means of mechanical devices for guiding the flame. Figure 228 shows the trimming of a locomotive driving rod by means of the oxyacetylene flame.   The temperature conditions at the cut surface are similar to those during fusion welding.

The carbon arc is also used for cutting, especially cast iron and alloy steels.   For a brief statement of the methods of coating, plating, and casehardening metals, see pages 317 to 320.

Selected Literature

"National Metals Handbook," American Society for Metals, Cleveland, 1939.
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THE HEAT-TREATMENT AND SURFACE TREATMENT OF METALS

HEAT-TREATMENT

General Considerations.—Heat-treatment of simple metals may be carried out advantageously (1) to harden and strengthen metals, (2) to relieve internal stresses, as in castings, (3) to soften objects for further working, or (4) to anneal objects previously deformed cold; also, (5) to spheroidize tiny particles, such as those of Fe_3C in steel, by diffusion, or (6) to impregnate the surface, as of steel, with carbon or nitrogen. The basic principles of the science of heat-treatment of alloys, to produce or to inhibit equilibrium in them, are developed in Part II, Metallography. The technology involved in carrying out these heating and cooling operations must include a study of the rate of heat flow from a hot metallic object to a bath during quenching, or from a furnace into a cold metallic object during heating. The object must usually be held at the high temperature until its temperature is uniform throughout and until equilibrium condi-
that temperature are approached. The extent to which a phase change may be inhibited by a quench depends, of course, on the velocities of the phase change in the temperature regions passed through in quenching and on the practically attainable velocity of heating or cooling of the object. If the phase change is a slow one, rapid quenching may inhibit it completely; for example, in 14 per cent Mn steel austenite may be retained at room temperature. If rapid cooling is not possible, as at the center of a massive object, the change may be only partially inhibited. In quenching thick objects, the properties of the metal at the center will be different from those at the surface, where cooling was more rapid, and are usually inferior to them. Thus in the heat-treatment of large forgings it is not always possible to obtain properties as good as can be obtained in small specimens and in test coupons. In the quenching of metal parts many problems of an

engineering nature are encountered. For instance, a long object, such as a shaft, if quenched horizontally will warp and may crack as a result of earlier cooling and consequent contraction of the bottom side of the shaft, which enters the bath first. In continuous quenching, the bath must be stirred constantly and kept at a constant temperature. Scale on the object may impede heat flow and produce soft spots in steel being hardened by quenching. Or bubbles of vaporized quenching liquid may insulate the object and, by diminishing the rate of heat extraction, produce soft areas. To avoid these vapor envelopes, the specimen, if very small, can be cooled more rapidly by "quench-
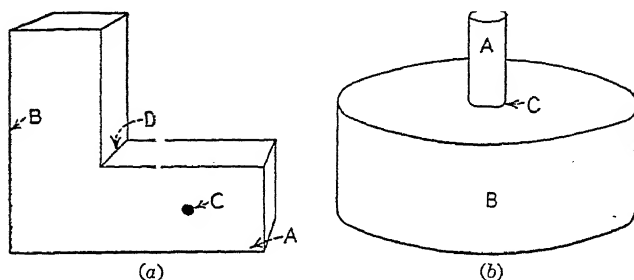
Fig. 229.—Rates of cooling in different parts of improperly designed objects for heat-treatment.

ing" in a stream of hydrogen. The cooling rate may reach 3000° per sec.[1] The dimensional changes accompanying the sharp temperature gradients and the phase transformations during quenching usually leave the metal in a state of high internal strain, frequently causing quenching cracks and later grinding cracks.

Design for Heat-treatment.[2]—An improperly designed object may crack either during rapid heating or during quenching because of the sharp temperature gradients and resulting high internal stresses set up in it during cooling. In an L-shaped object, such as is shown in Fig. 229a, the corner A is surrounded on three sides by air, so to speak, and thus is cooled on three sides. But it is heated from the interior on one side only. The

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[1] WEVER and ENGEL, *Mitt. der Kaiser Wilhelm Institute für Eisenforschung*, **12,** 93, 1930.

[2] PALMER, FRANK R., "National Metals Handbook," 1939.

SCOTT, HOWARD, "Some Problems of Quenching Steel Cylinders," *Trans. Am. Soc. Metals*, January, 1934.

corner will cool faster than the edge at B which is cooled on two sides and heated on two others. A point on the flat surface, such as C, receives heat from one side and dissipates it from the other. Point D is exposed on one side only to cooling action but is surrounded on three sides by hot metal. It will cool very slowly. The parts that cool most rapidly during quenching will usually heat most rapidly in a furnace.

Since the cooling rates are different in the different parts of the object, the specific volumes will be different and the cooling contraction will go on at different rates in different parts of the object, thus setting up internal stresses. The sharp angle at D will be the last to cool and the most likely to crack. This danger may be lessened if the angle D is replaced by a rounded fillet, which will prevent the concentration of stresses at the sharp angle.

If, in addition to having sharp angles, the object is massive in one part and thin or delicate in an adjoining part as shown in Fig. 229b, the difficulty is further increased. The light part A cools much more quickly than the massive part B, and it would be almost impossible to prevent cracking at the angle C even during quenching in oil. Similar difficulties would be encountered if heating up is too rapid in a furnace. In many cases sharp angles, as at the root of a gear tooth, cutting tool, or keyway, must be rounded off into a fillet. Parts that need not be heavy must sometimes be made heavy anyway, or massive parts must be made hollow to compensate for adjoining thin parts so that cracking will not occur.

Heating for Treatment.—The object may be charged cold into a cold furnace or cold into a hot furnace. Heating may be done in a variety of ways: in an open furnace, where the flames come into contact with the object being heated as in the soaking pit of a rolling mill; in an electric muffle; or immersed in a molten salt bath or a lead bath. The molten baths heat the object to their own temperature far more rapidly than an oven furnace will do. In these cases the surface of the object is hotter than the interior during heating. In some cases the object is heated by the passage of a heavy electrical current through the object itself. In this case the interior of the object usually is hotter than its surface. Rapid and nonuniform heating (or cooling) of objects of low heat conductivity may lead to

warping or cracking. Figure 230 gives the temperature differences between outside and center of a steel object of 50 cm. diameter under different conditions of heating in a furnace. The accompanying stresses set up in the object may be calculated from the coefficient of expansion of the material, the temperature gradient, and the modulus of elasticity.

Furnace Atmospheres. Pickling.—During heating, the outside of the object may be acted upon by the medium in which it is heated. Steels may be either decarburized or oxidized to form scale or both.[1] Scaling mars the finish and dimensions
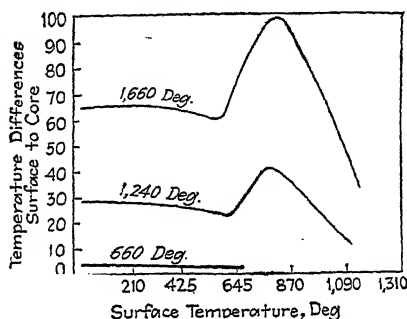
FIG. 230.—Surface temperature and core temperature for a piece of steel 50 cm. in diameter; for three different furnace temperatures. (*Rapatz in Sauerwald.*)

of the piece. Figure 231 shows a white layer of carbonless iron at the surface of an improperly annealed high-carbon steel rod. Obviously such a layer, being soft, would ruin a cutting tool, gear wheel, or die block. Scaled objects are usually pickled in dilute acid to dissolve the scale. Colloidal substances are frequently added to the pickling vats to inhibit attack of the metal beneath the scale.[2] Brass may lose zinc by vaporization. Nickel alloys, which must be annealed in a nonparticipating atmosphere, are very sensitive to gases that contain sulphur. Sulphur in the furnace gases forms brittle films of nickel sulphide at the grain boundaries, as shown in Fig. 232. The

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[1] See HEINDLHOFER and LARSEN, "Rates of Scale Formation on Iron," *Trans. Am. Soc. Steel Treating*, October, 1933; and J. A. WEBER, "Furnace Atmospheres and Decarburizing," *Trans. Am. Soc. Metals*, June, 1938.

See also James P. Gill, Campbell Memorial Lecture, *Am. Soc. Metals,* 1936.

[2] The hydrogen liberated from the acid sometimes enters the steel and causes it to be "acid brittle" until heated.

bright annealing of brass and other alloys likewise is done in a nonparticipating atmosphere, frequently propane or butane gas.

Copper ordinarily contains about 0.04 per cent oxygen as a Cu_2O eutectic at the grain boundaries. If it is heated in hydrogen, the oxygen is removed, rendering the grain boundaries weak. Hydrogen is used to remove carbon, sulphur, and phosphorus from iron by heating in a stream of this gas for a long time at a high temperature. Unburned fuel gas is commonly passed through the furnace to prevent scaling and decarburization of steel during heat-treatment. Nitrogen or dissociated ammonia also is used, and in rarer cases hydrogen, an inert gas, or a vacuum.

FIG. 231.—White shell of decarburized steel at the surface of a high-carbon rod.   (*Gregory.*)
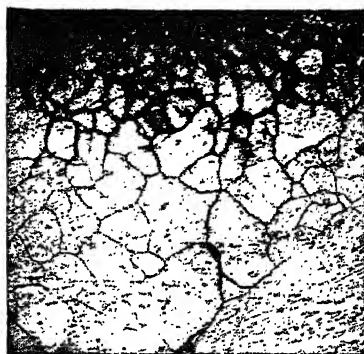
FIG. 232.—Sulphide envelopes in nickel heated in sulphurous gases. (*O. Schwarz.*)

Cold-rolled low-carbon steel sheets are frequently sealed in a large box before annealing. This measure preserves the surface finish. It is called *box annealing*.

The Function of Quenching Media.—The function of the medium into which heated metal objects are plunged is to withdraw the heat from the objects rapidly. The medium serves no other function, and the ancient practice of plunging a heated steel blade through a slave's thigh to harden the metal is an example of the needless suffering often caused by superstition. Even today superstition usually plays an important role in the choice of a quenching medium.

The rate of heat transfer from a hot metallic body into the quenching fluid, usually water or oil, depends upon the body itself—for example, upon its size and shape, its temperature, its

thermal conductivity, its specific heat, and the condition of its surface. The rate depends also upon the properties of the fluid—for example, its boiling point and latent heat of fusion, the conductivity and specific heat of its vapor phase, as well as the properties of the liquid phase, including its viscosity. The rate depends also on the temperature of the liquid and its velocity of motion past the hot object.

The matter can be simplified, however, by considering what actually happens when a red-hot steel object at, say, 750°C. is
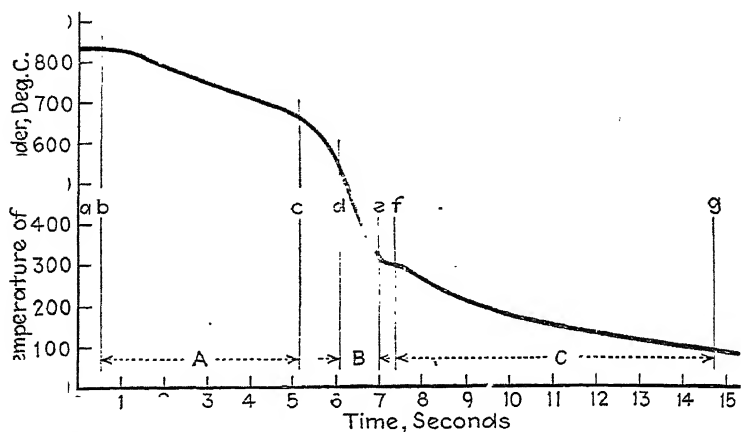
Fig. 233.—Rate of cooling at the center of a $\frac{1}{4}$-in.-diameter cylinder of 5 per cent silicon-nickel alloy quenched in still water. Note three stages of cooling. (*Pilling and Lynch.*)

plunged into stationary cold water. Under these circumstances the quenching action may be considered to take place in three stages, as follows.

Stages in Quenching.—1. In the first stage a continuous vapor blanket envelopes the entire surface of the specimen. In this stage no liquid touches the hot metal, and heat escapes from the hot surface very slowly by radiation and conduction through the layer of water vapor to the liquid-vapor interface. This is the period marked A on Fig. 233. It is undesirable in most quenching operations. Water cannot touch the hot metal because of the insulating film of vapor between, just as water on a hot stove does not "wet" the stove and, besides, is insulated from the stove by a vapor envelope. Heat extraction from the metal is quite slow in this first stage. This stage may be doubled or trebled in duration if the water be not cold but near its boiling

point. Hence, liquids of high boiling point are preferable in this respect. Thus, the addition of salt to water raises its boiling point and shortens the duration of this stage. If concentrated sulphuric acid is used, the first stage is entirely absent, owing, apparently, to the high boiling point of the acid. Soap added to water (as may happen when workmen wash their hands in the quenching bath) has the opposite effect, increasing considerably the duration of the first stage, possibly because the soap has stabilized the vapor-liquid interface and thus retarded the release of the vapor phase from the surface of the metal. Air dissolved in water is expelled on heating and may collect about the hot specimen. Sometimes the water to be used for quenching is boiled, to expel air.

2. The second stage of quenching is one in which the vapor blanket is broken intermittently, allowing liquid to touch the hot metal at one instant but soon being pushed away from it by vapor bubbles. The bubbles escape from the surface, and the liquid touches the metal again. This is the period marked *B* in Fig. 233. It is a period of very rapid cooling, as is indicated by the steep slope of the cooling curve. The rapid cooling soon brings the surface below the boiling point of the liquid, and the third stage of familiar cooling by convection of the liquid begins. If a high-pressure water spray is substituted for still water, the duration of the first stage may be shortened and cooling during the second stage may be greatly accelerated. The spray breaks up the vapor bubbles rapidly. For quenching the interior of hollow objects a nozzle is sometimes used. It will be noted that the second stage in Fig. 233 corresponds to the temperature region 600° to 500°C., in which steel in the austenite condition transforms most rapidly, as shown in Fig. 123, page 220. The rate of cooling in this stage is, therefore, of great importance in steel treating.

3. The third stage is one of cooling by simple convection and conduction of a liquid in contact with a metallic surface whose temperature is below the boiling point of the liquid.

In general, the quenching medium is of greater effect on metal objects of thin section. When the object quenched is massive, the rate of cooling in its interior will be proportional to the factor

$$\frac{\text{Thermal conductivity}}{\text{Density} \times \text{specific heat}}$$

This factor is called the diffusivity of the metal[1] and is only slightly influenced by the nature of the quenching medium.

Oil vs. Water.—In general steel-hardening practice, two distinct types of quenching media are required, one for parts that require superficial hardening, another for parts that must be fully hardened with little distortion. When superficial hardening is adequate and distortion is not a serious problem, plain carbon steels are used, because of their low cost and good machinability. A very rapid quench is necessary for these steels, and agitated water is the medium most frequently used.

For alloy steels, the rate of transformation and the temperature of transformation usually are lower than for carbon steels. Therefore, the rate of cooling need not be so high as it is for plain carbon steel, and thick objects of alloy steel can be hardened clear through, whereas plain carbon steels cannot. The greatest danger of cracking in quenching comes in the range of transformation of austenite into martensite. For avoiding this danger, cooling in that range (generally from 250° to 100°C., depending on composition) must be slow. Consequently, when full hardening is desired without the accompanying stresses, distortion, and the danger of cracking, oil at various temperatures may be used for the quenching medium, and its temperature can be held at about that of the martensite transformation range. However, since the cooling rate of oil-quenched material through the high-temperature range in which transformation takes place rapidly is slower than for water-quenched material, alloy steels, with their slower transformation rates, must be employed. Water frequently cools too rapidly in this range and results in warping and cracking.

_____ ___ ___ ____aples chosen here are for steel only, because its heat-treatment has received the greatest attention, it will be understood that the same principles apply equally to the cooling of other alloys in other media.

Tempering.—Subsequent to quenching, the temper may be partly withdrawn in the case of ordinary steel by "drawing" or annealing at some temperature lower than that from which the object is quenched. The effect is a partial release of the unstable condition (including internal stress) retained by

[1] For a more complete treatment see Howard Scott, Quenching Media, "Metals Handbook," 1939 ed., pp. 328–335, *Am. Soc. Metals.*

quenching.   In quenched plain steel a gradual softening results. In the age-hardenable alloys, such as duralumin, the metal hardens upon drawing—the so-called *artificial aging* (see page 229).   If quenching a steel object permits the retention of all austenite, as in Hadfield and other alloy steels, then drawing also is accompanied by hardening of the metal by allowing sufficient time for some of the soft austenite to transform to the hard, low-temperature product, martensite.

THE SURFACE TREATMENT OF METALS

Typical Methods of Surface Treatment.—The surfaces of metallic objects are sometimes coated with other metals or with fused oxides (porcelain or enamel) to prevent corrosion, or are impregnated with C or N_2 to make them hard.   Frequently a thin layer of alloys is thus formed between the coating and the base.   Gold is plated on brass, nickel on copper or iron, stainless steel on ordinary steel, "pure" aluminum on commercial aluminum.   Plates of the coating metal are sometimes welded upon thicker plates of the base metal (by either pressure- or fusion-welding methods), and the union is so tight that the composite object may be rolled into sheets, *rolled gold*, or drawn into wire without separation of the layers.   An intermediate layer may help the cohesion, as, for example, a tin coating on iron, which permits brass to be plated upon it, or copper and nickel on iron preparatory to a chromium plate.

Thinner coatings may be applied by dipping the previously cleaned object into a molten metal, as steel into molten zinc (*galvanizing*), tin, or lead.   The liquid metal diffuses into the surface of the object to some extent, as shown for iron and zinc in Fig. 234a, and forms thin layers representing all of the intermediate alloys between pure iron and pure zinc, as shown by their equilibrium diagram.   Some of these alloy layers, being intermetallic compounds—*e.g.*, $FeZn_7$—are quite brittle.   The object may be heated in a zinc powder (*sherardizing*) or in an aluminum powder (*calorizing*) to produce a coating of the second metal.   Here, too, very thin layers of intermediate alloys form by diffusion of the second metal into the object.   Steel castings with a stainless-steel surface are made by coating the interior of the mold with a ferro-chromium "wash" before casting.   The

laws of diffusion, as presented on page 211, govern the formation
of the bond between the coating and the base metal.

At room temperature, coatings may be applied by electrolytic
deposition (*electroplating*), as of nickel, chromium, etc., upon

FIG. 234a.
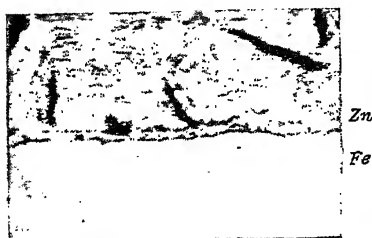
FIG. 234b.
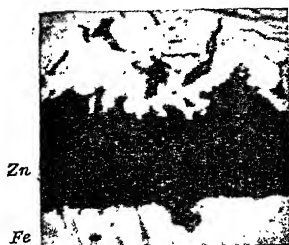
FIG. 234c.
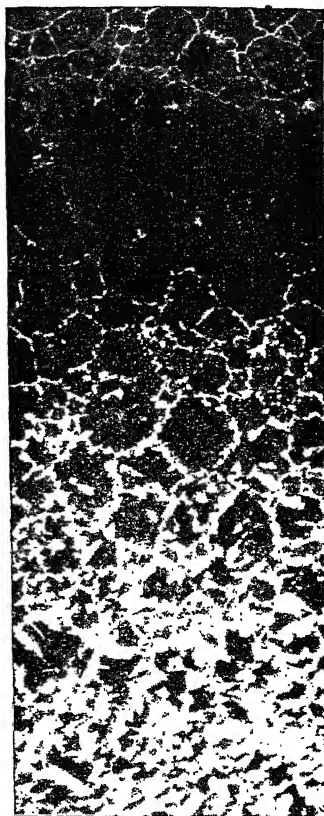
FIG. 235.

FIG. 234a.—Section of "hot-dipped" galvanized sheet.   × 100.
FIG. 234b.—Section of electrolytic zinc deposit on iron.   × 100.
FIG. 234c.—Section of a sprayed zinc coating and base.   × 100.
FIG. 235.—Microstructure showing carbon content of a carburized case.   Top
of figure which is the surface of the object about 1 per cent carbon; black region
0.85 per cent carbon; bottom about 0.30 carbon.

iron.   In this case very little if any alloy layer is formed between
object and coating.   Figure 234b shows an electrolytic deposit
of zinc on iron.

Electrolytic deposits of aluminum on iron are also obtained
in a fused electrolyte of $AlCl_3$ + NaCl.   If a coating is broken,

local cell action between the coating and the base metal may be set up. If the coating is cathodic to the base metal, as in tin or nickel on iron, the base may corrode more rapidly than it would if no coating were present. The corrosion resistance of steel is improved by treatment in a phosphate solution (*parkerizing*), which forms a protective oxide layer, see page 272.

In some processes, as in the Schoop process, liquid metal is sprayed against the previously sand-blasted surface of the object while cold, where it clings more or less tightly. No diffusion takes place (see Fig. 234c).

Carburizing, Nitriding, and Cyaniding.—The processes for hardening the surface through impregnation, as of soft steel after it has been machined to size, by diffusion of C or N_2 inward from the surface, include case carburizing, nitriding, and cyaniding. The metal at and just below the surface combines with the impregnating material to form a hard alloy, iron carbide or iron nitride. In the case of carburizing, iron or steel objects are packed in bone charcoal with a catalyst, usually a mixture of alkali carbonates, and heated for several hours at a temperature of 900°C. or more. The carbon diffuses into the iron under the force of the high-carbon concentration gradient from the surface to the interior. The depth of the resulting case is dependent upon the temperature because of its effect upon the rate of diffusion and the reaction rate, upon the time allowed for the reaction and diffusion to take place, and upon the composition of the gas generated in the carburizing box. The effect of the catalyst is to increase the CO to CO_2 ratio and consequently hasten the reactions, which seem to be

$$2C + O_2 \rightarrow 2CO$$
$$3Fe + 2CO = Fe_3C + CO_2$$
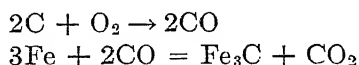
The iron must be in the austenite range, because only in austenite has C any appreciable solubility. The core of the object remains unchanged in carbon content as illustrated in Fig. 235. Carburizing may also be accomplished by the use of carbon-bearing gases. By suitable heat-treatment a case-carburized object may become very hard at its surface but remain ductile and tough throughout most of its cross section. Nitrogen from the decomposition of NH_3 will cause hardness on the surface of an iron object as the result of the formation of iron nitrides at

525°C. after 90 hr. If the iron contains a small amount of aluminum (*nitralloy*) as catalyst, the reaction is accelerated. Nitride cases need no subsequent heat-treatment, as do carburized cases, and hence do not lose their shape by warping. The relative hardness and depth of these two cases are shown in Fig. 236. Heating in fused sodium cyanide introduces both carbon and nitrogen. It is called *cyaniding*. The case formed is very thin. Diffusion sometimes progresses more rapidly along the grain boundaries, as of hydrogen into steel, or of solder into stressed brass, than it does *through* the grains.[1]
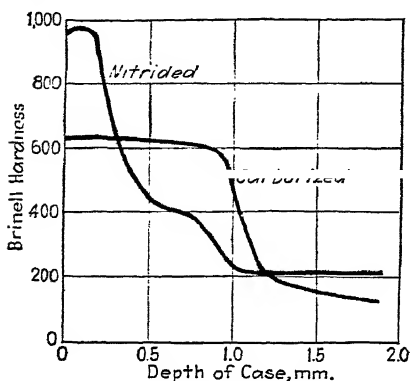
FIG. 236.—Hardness of nitrided and carburized cases at various depths below the surface. (*O. Schwarz.*)

Artificial Surface Films.— The surfaces of metallic objects may also be colored by certain chemical treatments as, for instance, oxidation in the presence of steam or by immersion in a bath of fused nitrate, to produce a "blued" steel. The color is due to interference in the light waves reflected from the surface of the film and from the metal beneath the film. A variety of colors may be obtained in this way by varying the thickness of the film. Gun-metal finish is obtained by dyeing the oxide film with a logwood solution. Other dyes may be used for other colors. (See, also, page 272, Prevention of Corrosion.)

The film of oxygen on "passive" iron after exposure to anodic oxygen, and the spontaneous but invisible oxide film on chromium plate, stainless steel, and aluminum, are also examples of protective coatings. Such films are sometimes produced artificially by anodic treatment of the part to be protected—*e.g.*, on duralumin by anodic treatment in a chromic acid cell.

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Heat Treating Forging.

See also Selected Literature at end of Chap. IV.

CHAPTER XI

THE TESTING OF METALS

Types of Tests.—The properties of metals that are most important as far as their use is concerned are their mechanical properties. On the one hand, service conditions require that metals resist a great variety of stresses without undergoing appreciable deformation. On the other hand, fabrication processes demand that metals be capable of deforming in a variety of ways with comparative ease, so that they may be formed into the shapes required by consumers. Consequently, tests are designed for two purposes: (1) To determine the effective resistance of metals as regards service stresses, and (2) to determine the formability of a metal for a given fabrication process. A third type of testing may be mentioned, which has to do with the homogeneity or soundness of the object as a whole (nondestructive: radiographic, electrical, and other methods).

Tests may be generally divided into two classes: (1) Those that attempt to simulate service conditions as nearly as possible, *e.g.*, the actual use of experimental parts in service or fabrication processes, or the setting up of pilot plants for determining the general suitability of materials; and (2) those designed to study the behavior of metals under specified conditions not necessarily related to specific service or fabrication, *e.g.*, the tensile, hardness, and impact tests. The first class of test is the most satisfactory, but it is also usually expensive, elaborate, and slow. Therefore it is not widely used. The second class of test, which is more generally used, is based on the fact that, although the conditions of the test are not necessarily related to those to be encountered in service, the behavior of the metal in the tests ultimately depends upon the same properties that determine their usefulness. Care must be exercised in the selection and interpretation of such tests. The latter type of test is also widely used to study the fundamental properties of metals (cohesive strength, deformation mechanisms, etc.).

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The tension test will be considered first. It will serve as a good example of the general case of mechanical testing. Let us first examine a very general tensile curve that will illustrate the principles and then consider the very important specific case of the tensile test for steel.

In the tensile test a specimen of uniform cross-sectional area is subjected to a progressively increasing tensile pull until it fractures. The metal deforms appreciably as long as the stress is increased and stops deforming when the load is held constant. If the stress (load divided by the original cross-sectional area) is plotted against elongation (exten-

Fig. 237.—A diagrammatic stress-strain curve to illustrate the general principles involved in the tension test.

sion between gage length on specimen divided by the original gage length), the so-called *stress-strain* diagram is obtained. Figure 237 is the diagrammatic general curve that we shall use to discuss the principles involved.

The first deformation OW in the figure is proportional to the applied stress. This condition is expressed by Hooke's law, $e = Pl/AE$, where P/A is the unit stress, l is the original length of the specimen, and E is the modulus[1] of elasticity. When the load is removed the specimen returns to its original dimensions. The highest stress which the specimen can sustain and still return to its original dimension when the stress is removed, is called the elastic limit. Elasticity may persist after proportionality has been exceeded. In the case of some nonferrous metals, this effect is quite marked. As we stated on page 84, the elastic limit is evidently a quantity dependent in magnitude upon the sensitivity of the measuring instrument, and from a scientific standpoint may not exist. Fe and Ni have appreciable elastic limits, but Cu, Al, Zn, Sn, and Pb have limits of approximately zero.

As soon as the elastic limit is exceeded, plastic deformation and the accompanying work hardening begin. The shape of

[1] The modulus of elasticity is the stress intensity which would be necessary to produce an elastic elongation e, equal to the original length l. For steel it is about 30,000,000 lb. per square inch. E for a number of metals is given in column 7, Table III, page 62.

the remainder of the curve is primarily dependent upon the rate of work hardening. As deformation proceeds, a point is reached where the deformation increases rapidly with a slight increase in load. Such a point is called the yield strength (*b* in Fig. 237). Arbitrarily a deformation 0.2 per cent is usually allowed at the yield strength. The specimen continues to deform with increasing stress until the point *d* (ultimate strength) is reached. The load decreases thereafter until fracture. The elongation on deformation is accompanied by an ever-decreasing cross-sectional area, termed *reduction in area*, and when it is realized that stress is calculated by dividing the load by the *original* cross-sectional area, it is easy to see that such a calculation does not give the true stress but a stress below the actual amount, depending upon the extent of reduction of area. As we shall see later, if the *actual* unit stress is calculated, the specimen will fracture at the maximum stress rather than at a low stress, as indicated by the conventional diagram.

The shape of the curve as shown depends upon the relationship between the rate of work hardening and the rate of reduction of area. As long as the load is increasing with deformation, the rate of work hardening is balancing the rate of reduction of area, and the elongation   and uniform. When the load decreases with deformati   ie rate of reduction in area exceeds the rate of work harde   ie deformation becomes localized, the specimen necks do   rapidly and fractures. When the load is removed by fra   ire (*e* in Fig. 237), the elastic part of the deformation *ZZ'* is rec   ·ed. From this fact it must be inferred that elastic deform   ontinually accompanies plastic deformation and is recovered . lenever the load is removed.

Figure 238 shows the stress-strain curve for a mild steel. This curve exhibits a comparatively large proportional range, the limit being indicated by *PL* on the diagram. The load at which the proportionality disappears, divided by the original cross-sectional area, is termed the *proportional limit*. During tension, the change in dimensions—*i.e.*, reduction of area and elongation—is such that the volume decreases slightly. The ratio of per cent change in diameter to per cent change in length is called *Poisson's ratio*.

When the stress is further raised to a point somewhere above the proportional limit, the metal suddenly begins to flow rapidly

without any increase in load. In fact, if the rate of loading is slow, the specimen may yield faster than the load can be applied and the result may be a sinking of the load. This initial point of rapid flow is the yield point of steel. The flow at the yield point is local in nature; it starts in one area and spreads throughout the entire piece as each successive localized area work-hardens. This localized yielding results in stretcher strains or worms in mild steel sheet, as illustrated in Fig. 88, page 109. As soon
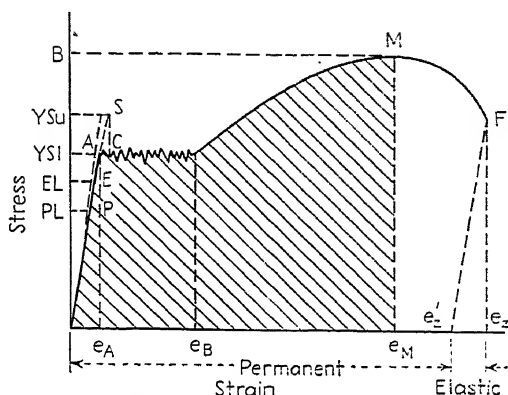
FIG. 238.—Stress-strain diagram of mild steel showing double yield point and "spring back."

as the entire piece has been strengthened as a result of this progressive local yielding, the stress again begins to rise and the deformation again becomes uniform. When the point M is reached, the rate of reduction of area again exceeds the rate of work hardening, the specimen necks rapidly, the load falls, and the specimen fractures. The load at M, divided by the original cross-sectional area, is called the *tensile strength* of the material.

"Spring Back."—When the stress is removed from the specimen, either by fracture or in stamping and deep drawing, the elastic portion of the deformation disappears, as is shown at the lower right in Fig. 238. Die designs for stamping metal objects must provide for this "spring back" if accurate dimensions are desired.

Specimen Dimensions.—In order to obtain comparable results, these properties, especially reduction of area and elongation, must be measured under certain conditions. The dimensions of several

standard tensile specimens are given in Fig. 239. As long as the test length of the specimen is equal to a constant times the square root of the area, the results will be independent of the size of the test specimen. Usually the condition $l = 4.5 \sqrt{\text{area}}$ is adopted. Not only the dimensions of the specimen but also the rate of application of the load and the temperature influence the results
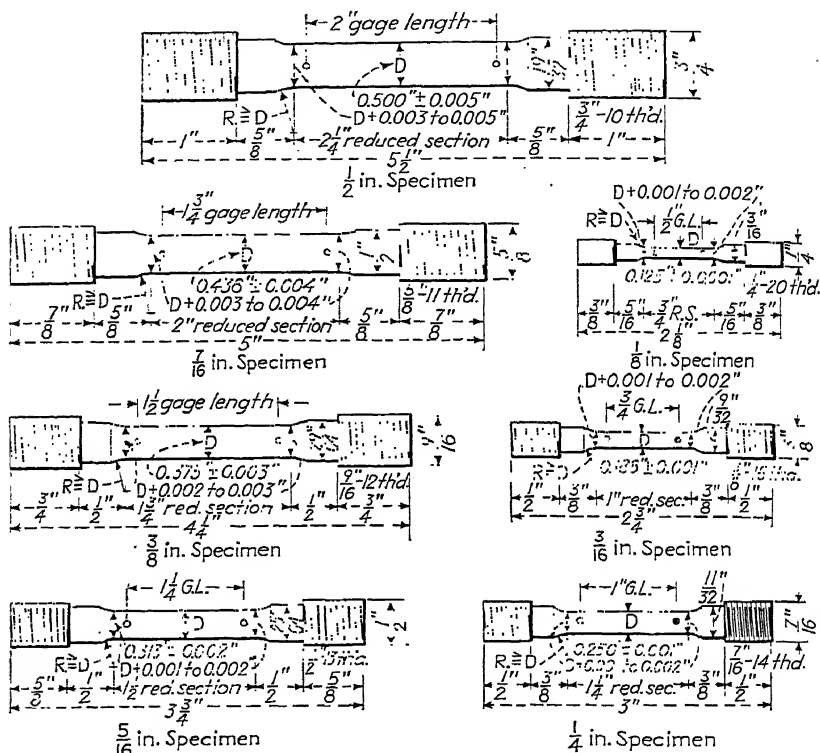
Fig. 239.—Various sizes of threaded end, round tension test specimens for metals. ("*Metals Handbook*," *American Society for Metals*, 1939.)

that are obtained. Rapid loading, for instance, gives higher strength. If the neck should occur not in the middle of the test length but near the ends, the values for elongation and reduction would be low, owing to the support received from the ends, and a retest would be required. With flat strip specimens, the reduction and elongation are lower, the wider the specimen. Figure 240 shows the stress-strain diagrams of a 0.3 per cent carbon steel after various heat-treatments.

. **The compression test** reverses the direction of the forces used in the tension test. The stress-compression diagram for several metals is shown in Fig. 241. In this test the stress rises rapidly near the end of the test, owing to an increase in area of the specimen, instead of a decrease as in the tension test. The compression fracture in a brittle material, as cast iron, is shown in Fig. 242. The specimen selected depends upon the metal being tested. For bearing metals it is usually a cylinder whose
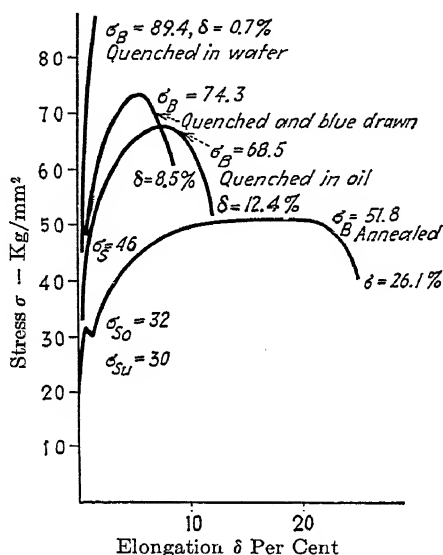
FIG. 240.—Stress-strain diagrams of a 0.3 carbon steel after various heat-treatments. σ_B = tensile strength; δ = elongation.

height is equal to its diameter. To determine general compressive properties, a specimen is usually chosen in which the length is three times the diameter. If the material is plastic instead of brittle, it bulges at its mid-section, owing to the greater friction to flow at the top and bottom surfaces. This condition is diminished by lubricating these surfaces or by machining a cone-shaped depression in the ends of the specimen.

The Bend Test.—In this test the specimen is loaded as a simple beam, as in Fig. 243. It is used chiefly for brittle materials, in which case it may serve also as a simpler substitute for the tension test. It may well be used as a good shop test for acceptance purposes, but not for research purposes. The tensile strength

in bend, based on the stress in the outermost fibers of the specimen of length l, can be calculated as follows:

$$S = \frac{Plh}{4 \cdot 2\theta}$$

where S is the modulus of rupture, P is the load, h is the height (depth) of the specimen, and θ is the moment of inertia of the section (for rectangular bars $\theta = Wh^3/12$, where W is the width; for circular sections $\theta = \pi d^4/64$, where d is the diameter). The assumption necessary is that the deformation of the outermost
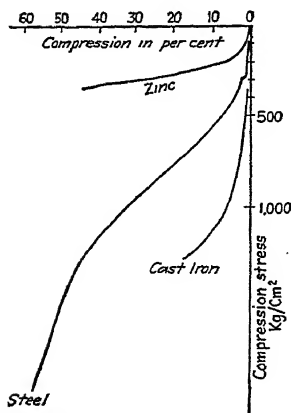
FIG. 241.—Stress-compression diagrams. (*Sachs.*)
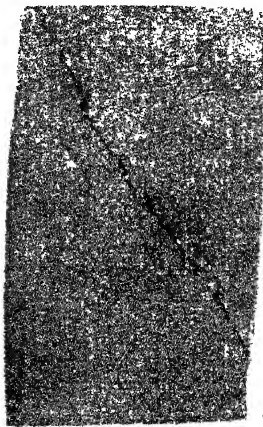
FIG. 242.—Compression fracture in cast iron. (*Wawrziniok in Sauerwald.*)

fibers is proportional to the stress. Obviously, there is some plastic flow in these fibers, which relieves the stress. This leads to high values for all materials, but the results are fairly good for brittle (nonplastic) materials. Formability is measured in the bend test by the angle at which fracture begins.

The Torsion Test.—The torsion test consists in twisting a specimen, as shown for an extremely plastic material in Fig. 244. Aside from its intrinsic uses, the specimens from such a test are useful in that they supply material for experiment in all degrees of deformation, from zero at the center of the specimen to a maximum at the exterior.

Hardness Testing.—Hardness testing is carried out in various ways. The most common is the ball-impression method. The

ball, or penetrator, is pressed into the surface of the material with a certain force, and the amount of penetration produced in relation to the load is used as a measure of the hardness.

In the *Brinell test* a hardened steel ball is pressed into the surface being tested. Naturally, if the hardness of the surface approaches that of the ball, the results are inaccurate. The Brinell hardness number is expressed as the ratio of load to area of the surface of the impression; but a certain ratio of load to diameter of ball must be maintained in order to get concordant results. A ball of 10 mm..diameter is generally used and pressures of 3,000 kg. for steel or 500 kg. for softer metals, respectively. If a 5-mm. ball is used, loads one-quarter those given for the 10-mm. ball would be used. The hardness numbers remain more or less constant if the load is proportional to the square of the diameter of the sphere. The time of subjection
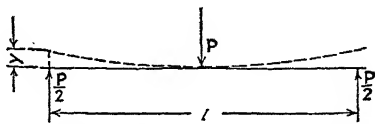
Fig. 243.—The bend test. (*Wawrziniok in Sauerwald.*)

Fig. 244.—Torsion specimen after twisting.

of the load must be constant, usually 30 sec. Naturally the impression must not be made near the edge of a specimen. (The Brinell hardness of a number of common metals is given in column 8, Table III, page 62.) The hardness test is sometimes used as a substitute for the tension test to measure resistance of the metal to deformation. The correlation is a limited one, however. The *Vickers hardness test* is similar in principle, but it uses a diamond indenter in the shape of an inverter square-based pyramid.

The *Rockwell test* uses either a ball, or a diamond cone with 120-deg. angle. The penetrator is first loaded with 10 kg. and the indicator set at zero, as shown at the left in Fig. 245. The load is then raised to 150 kg. The depth of impression is meas-

ured automatically after the latter load is removed.   These conditions are shown diagrammatically .n Fig. 245.   For softer metals the second load may be set at 100 kg. or 60 kg. instead of 150 kg.

The *scleroscope* measures the height of rebound of a tiny, diamond-tipped tup after it falls upon the surface of the specimen.

Rockwell hardness tester
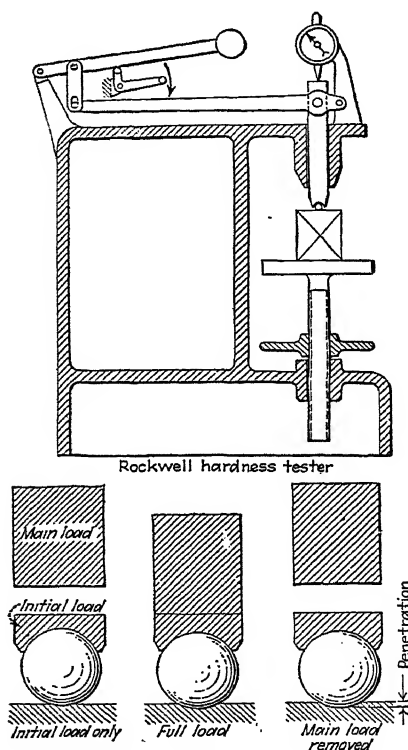
Fig. 245.—Cycle in Rockwell hardness testing.   (*Deutsch.*)

Hard rubber appears harder than steel in this test, but the test has many uses.

The Scratch Test.—The *scratch hardness* is determined by drawing a diamond point, loaded with a certain load, over the surface of the metal to be tested.   The width of the scratch is a measure of the hardness of the material; or the load may be adjusted so as to give a scratch of standard width, in which case the load required is a measure of the scratch hardness of the

material. Figure 246 gives a relationship between various hardness tests.

Obviously the metal is .deformed in all these tests, and the deformation increases the hardness of the metal. Hence, metals that work-harden rapidly will give higher hardness values than those that do not.

Erichsen Test.—Special tests are designed to simulate the stresses to which metals are subjected in special industrial
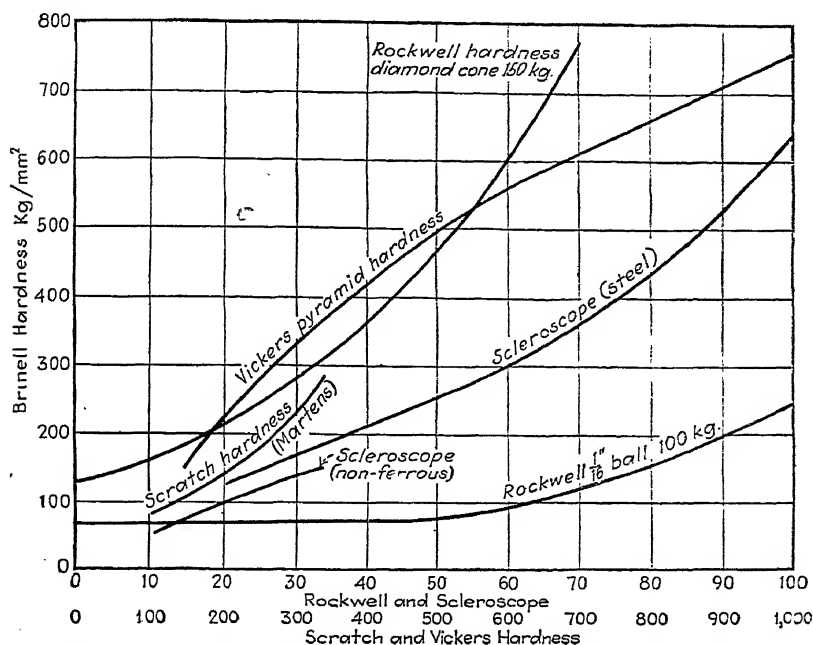
FIG. 246.—Brinell hardness equivalents (approximate).   (*O. Schwarz.*)

operations. For instance, in the deep drawing of steel sheets into automobile fenders and tops or into cups, the Erichsen test will indicate the suitability or nonsuitability of a certain batch of metal for this purpose. A small piece of the sheet is pressed by a rounded mandrel into a cup-shaped die. The depth of the cup so obtained, without cracking, is a measure of the deep-drawing qualities of the sheet tested. Large grain size seems especially undesirable in sheet for this purpose. Steel sheets have sometimes been found to age-harden and gradually to

become unsuitable for deep drawing. Recent developments and one significant invention have diminished these difficulties.

The Charpy Test.—Frequently metallic objects must resist sudden shocks in service. Tests simulating these shocks, *e.g.*, the notched-bar test, are used to measure this property of shock resistance. A standard *Charpy* specimen is shown in Fig. 247a. The pendulum falls and strikes the specimen opposite the notch, midway between the supports as shown in Figs. 247a and b. The arc traveled by the pendulum after fracture for the specimen indicates what fraction of the initial energy of the pendulum was
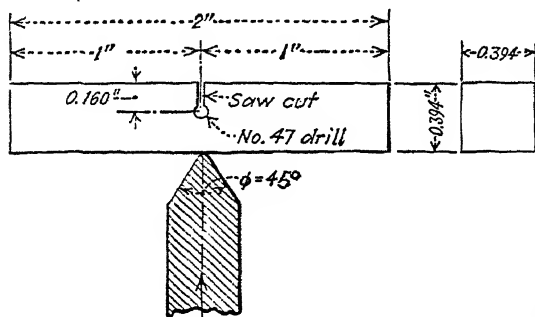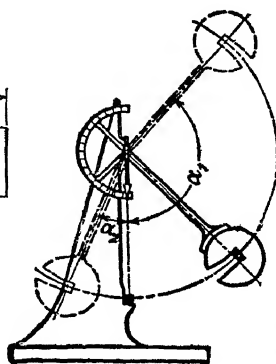
Fig. 247a.   Fig. 247b.

Fig. 247a.—Charpy impact specimen and pendulum face.
Fig. 247b.—Charpy impact apparatus showing three positions of pendulum.

absorbed in fracturing the specimen. The *Izod* test is similar, except that one end of the specimen only is gripped. The *notch toughness* is expressed as the energy absorbed in rupture divided by the area of the fracture. Steels high in phosphorus appear brittle in this test although they may show good elongation in the slow-tension test. The notched-bar test is useful also in controlling the heat-treatment of nickel steels.

Other methods of dynamic testing include an impact tension test, an impact compression test by means of a simple gravitational hammer, and an impact or pendulum hardness test, the last using either the height of rebound of a falling weight (Shore scleroscope, Duroscope) or the volume of the indentation produced.

The detailed instructions for carrying out tests of this kind can be found in a handbook, such as the "National Metals Hand-

book" of the American Society for Metals or in the *Proceedings* of the American Society for Testing Materials.

Fatigue Testing.—Repeated alternating stresses, even as low as one-half the elastic limit of a material, may ultimately result in failure if the stress is repeated often enough. Such failures are known as *fatigue failures*. They may occur in engine or machine parts, such as axles and shafts, in bridges, transmission wires, and other parts subject to vibration. If the unit stress is reduced to a low value, the number of cycles of stress before failure increases and seems to become infinite. The highest unit
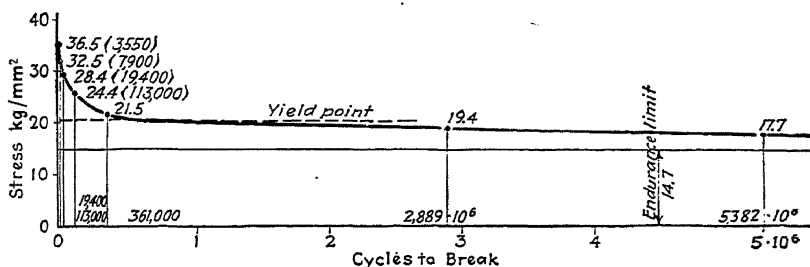
Fig. 248.—Fatigue diagram of a 0.08 per cent carbon steel; tensile strength 36 kg. per square millimeter. Yield point 21, endurance limit 14.7. (*O. Schwarz.*)

stress compatible with this condition of long life is called the *endurance limit* of the material.

A common method by which tests of metals are carried out to determine their endurance limits is rotation of a standard specimen, loaded either as a simple beam or as a cantilever. At any instant the fibers at the top of the cantilever are in tension; those at the bottom, in compression. An instant later, when the specimen has rotated 180 deg., the stresses are reversed. The maximum unit stress in the outermost fibers is calculated, and the number of cycles of stress required to produce fracture is recorded by a cyclometer attached to the testing machine.

The relation between intensity of unit stress in the specimen and number of cycles to produce fracture is shown in Fig. 248. At high unit stresses, fracture occurs after very few cycles. As the unit stress is decreased, the life of the specimen increases until finally at a low stress, known as the *endurance limit*, the specimen may run for 10,000,000 cycles or more without fracture. The curve becomes asymptotic to the time axis.

Acceleration and Retardation of Fatigue Failure.[1]—The presence of machining scratches on the surface of the specimen, and, for most metals, the corrosive action of water on it during test, both lower the endurance limit out of all proportion to expectation. For these reasons, machine parts should be carefully machined and should be as free as possible from keyways,
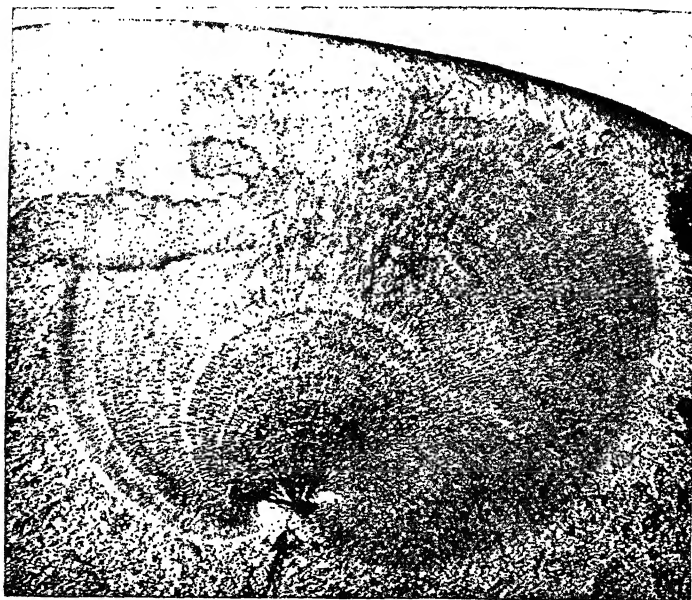
FIG. 249.—Fatigue fracture which originated in a slag inclusion (see arrow) in a sheet roll.   × ½.   (*Oberhoffer.*)

sharp fillets, and machining scratches. Furthermore, if the part runs in contact with water, a protective coating—*e.g.*, one of zinc—is frequently desirable.

The failure of metals at these low stresses is usually attributed to the concentration of stress in regions of inhomogeneity in the metal, such as slag inclusions or a corrosion pit, and the progressive extension of a crack beginning at one of these points and progressing throughout the specimen. The radial appearance of a fatigue break that originated in a flaw is shown in Fig. 249.[2]

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[1] "Prevention of the Failure of Metals Under Repeated Stress," Battelle Memorial Institute, John Wiley & Sons, Inc., New York, 1941.

[2] See also FRENCH, H. J., "Fatigue and the Hardening of Steel," *Trans. Am. Soc. Steel Treating,* October, 1933.

Corrosion Fatigue.—Where corrosive action occurs simultaneously with fatigue stress, the condition is commonly called *corrosion fatigue*. The flexing action of the metal seems to break up possible protective films at the root of each corrosion pit, and corrosion progresses unimpeded; the result is that very deep pits are formed, with an accompanying intensification of stress at these pits. The life of automobile valve springs may be only one-sixth of the expectancy, owing to corrosion by crankcase gases and the water condensing from them. For steel, heat-treatment or cold working improves the endurance limit in air in
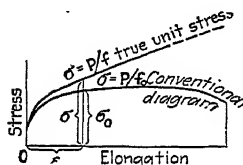
FIG. 250.
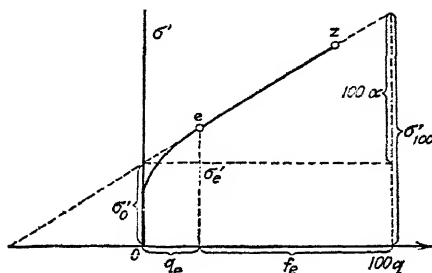
FIG. 251.

FIG. 250.—Rational and conventional stress-strain diagrams. (*Nádai.*)

FIG. 251.—Actual unit stress *vs.* reduction of cross-sectional area.

(Abscissa = per cent reduction of area; ordinate = actual unit stress.)

proportion to improvement in the elastic limit. It seems to have little effect on the corrosion-fatigue limit.

Rational Interpretation of Results of Physical Tests.—Obviously, the tensile strength obtained by dividing the maximum load by the *original* area of the specimen is not a measure of the true stress on the material. The *final* load divided by the *actual* area at fracture would, however, approximate it. If the actual unit stress—*i.e.*, the instantaneous load divided by the accompanying instantaneous sectional area—is plotted against the instantaneous elongation, as in Fig. 250, we find that the unit stress rises continuously during the test, instead of reaching a maximum and then falling. The curve for the same material in the compression test is similar, especially if the specimen contacts are lubricated.

The actual stress may likewise be plotted against percentage reduction of area given in Fig. 251. The point *e* corresponds to the maximum total load during test, and also to the load at which a neck begins to form. From this point on, the rise in

actual stress per unit of actual sectional area of the specimen at this stress is nearly linear. The slope of this line is a first approximation of the *work hardenability* of the material, since the unit stress in the specimen can rise only as the metal hardens. Prolongation of this line to the stress axis indicates the yield point of the material. For annealed material, calculations show that the stress at the point *e* is a half of the stress which would exist at 100 per cent reduction of area.

The true work hardenability is found by subtracting from the observed hardening the part that is due to change of shape of the specimen at the neck. This part can be determined by machining necks in separate specimens to get the
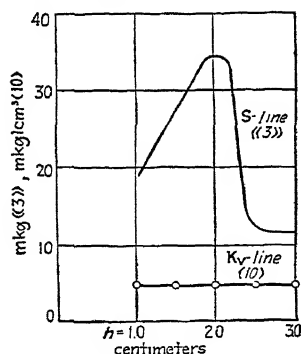
Fig. 252.

Fig. 253.

Fig. 252.—Line K_v shows energy absorbed per cubic centimeter of metal deformed; line S per square centimeter of fractured section, for various widths of specimens. (*Moser in Sauerwald.*)

Fig. 253.—Deformed region (lighter) at notch in Charpy specimen. (*Moser in Sauerwald.*)
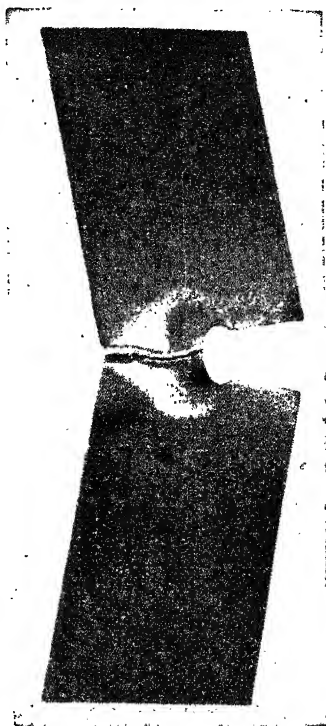
"shape-hardening" influence. It is found that the latter factor is relatively small for plastic materials.

The notched-bar test gives scattered results when the energy absorbed in fracture is divided by the area of fracture, but quite constant results if the *volume* of metal deformed by fracture is used. The results, related to the width of the specimen, are shown in Fig. 252. The volume of metal deformed is readily

measured, as indicated by the lighter area in Fig. 253. The volume of deformed material depends on the velocity of fracture. It is smaller, also, for brittle materials than for tough ones. This leads to the conclusion that brittle materials are those that can
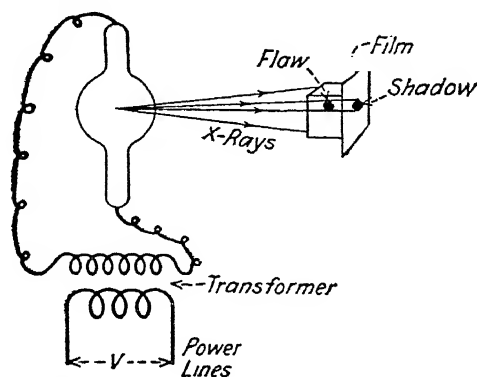
FIG. 254a.—X-ray radiographic testing. (*Doan.*)

develop a large volume of deformation only when the rate of deformation is slow and when the width of the specimen is small.

Testing for Homogeneity. Radiographic Testing.—Electromagnetic rays of short wave length, such as X rays and γ rays, penetrate "opaque," "solid" matter as if it were translucent. If a metallic object—say, a casting or a weld containing cracks, slag, or gas cavities—is placed in the path of such rays, the rays pass through the object. The rays emerging from the object in line with such flaws will be more intense than the rays that traverse solid metal. A photographic film

Gamma Ray Testing

FIG. 254b.—Gamma-ray testing.

(in a container impervious to visible light) placed behind the object will be blackened, but more intensely blackened in line with each flaw. It is thus possible, without cutting an object or in any way destroying it, to detect flaws in the interior of the object merely by passing invisible rays through it and registering[1,2] them on a film behind it. Figures 254a and b show diagrammatic views of the two methods. Figure 255 shows cracks revealed by

[1] MEHL, DOAN, and BARRETT, *Trans. Am. Soc. Steel Treating*, 1930.

[2] DOAN, *J. Franklin Inst.*, August, September, 1933.

gamma rays in the interior of a steel casting 7 in. thick.   X rays cannot be used for sections of steel above 4 in.

Magnetic Test.—If a nonhomogeneous object is magnetized and its surface is sprinkled with iron filings, the filings will collect at a crack or void (often invisible otherwise), owing to the intense field (north and south poles) at the discontinuity.   Airplane crankshafts are now removed from their engines and tested in this manner at stated intervals in order that fatigue cracks may be
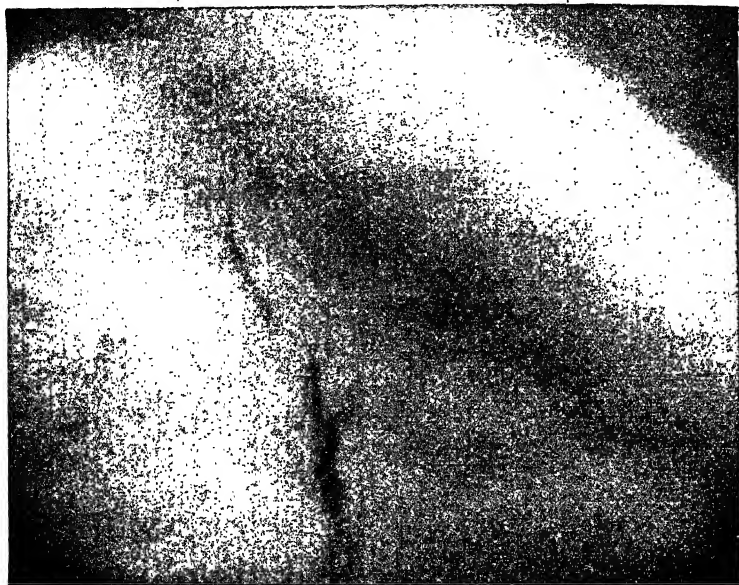
FIG. 255.—Cracks in steel 7 in. thick as revealed by gamma rays.   (*Mehl and Barrett.*)

detected before they have progressed far enough to cause an accident.

Electrical Test.—If a heavy current is sent through a homogeneous object, as for instance a railway rail, the object will be surrounded by a uniform magnetic field.   A coil of wire moved along in this field will have a current induced in it.   If, however, there are flaws in the object, such as transverse fissures in a rail, the axis of current flow will deviate at these points and the exploring coil will register a change in induced current, indicating the location and magnitude of the flaw.   This device may be run along a railroad track at about 6 miles per hour and made to

register on a chart the flaws in the rails passed over. The "flaws" at a rail joint are discounted.

Important conclusions about the properties of a metal may, of course, be drawn from examination of the polished and etched section, as discussed elsewhere. Internal stress and reorientation as well as grain size may be determined by means of X-ray diffraction methods, also described elsewhere in this treatise.

The macroetch test consists of subjecting the surface of a metal section to the action of an acid, frequently a 50–50 HCl-water solution, at 160°F. for a period usually from 15 to 45 min. Such etching reveals to the naked eye such defects as seams in rolled material, surface cracks, internal shrinkage cracks, pipes, segregations, and dendritic patterns.[1]

Spark Test.—The approximate carbon and alloy compositions of steels may be estimated in the hands of an expert by observation of the shape and color of the sparks emitted when the steel is pressed against a grindstone in a dark room. This method is called *spark testing*.

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[1] "National Metals Handbook," American Society for Metals, Cleveland, 1939.

CHAPTER XII

COMMERCIAL ALLOYS, PROCESSES AND PROBLEMS

General.—Seven metals only are used in quantity for engineering construction. They are iron, nickel, copper, aluminum, zinc, tin, and lead. It is beyond the scope of this text to treat fully even the most important alloys of each of these seven metals. It is important, however, for the student to know what these commercial alloys are and to have mentioned to him the basic processes and problems involved in their use, so that he may see as clearly as is possible how these processes and problems are related to the fundamental principles developed in the earlier pages of this text. The ability to recognize the principle that is involved in a problem, or, as it is commonly put, the ability to apply principle to practice, is as necessary to the engineer as is the knowledge of principle itself.

While it is thus desirable to give some brief notice to the industrial alloys in the same text that discusses the fundamental principles, nevertheless, when the student or the engineer reaches a point in his career where he wishes to concern himself in detail with alloys of one type, the steels or the brasses or the aluminum alloys, for instance, he will turn to a separate book devoted to those alloys. A number of books of that kind are noted at the end of each section of this chapter. No attempt will be made here, therefore, to record the mass of experimental data or empirical recipes and formulas that has accumulated in the field of each of the commercial alloys. Rather, the aim will be merely to indicate the way in which the fundamental principles of physical metallurgy are related to them.

The Commercial Alloys.—Before treating separately the alloys of each of the seven common metals, let us survey the alloys used industrially, grouping them in their natural families in the periodic system of the elements. Figure 256 shows the diagrams of the most important binary alloys of each of these seven metals.

340
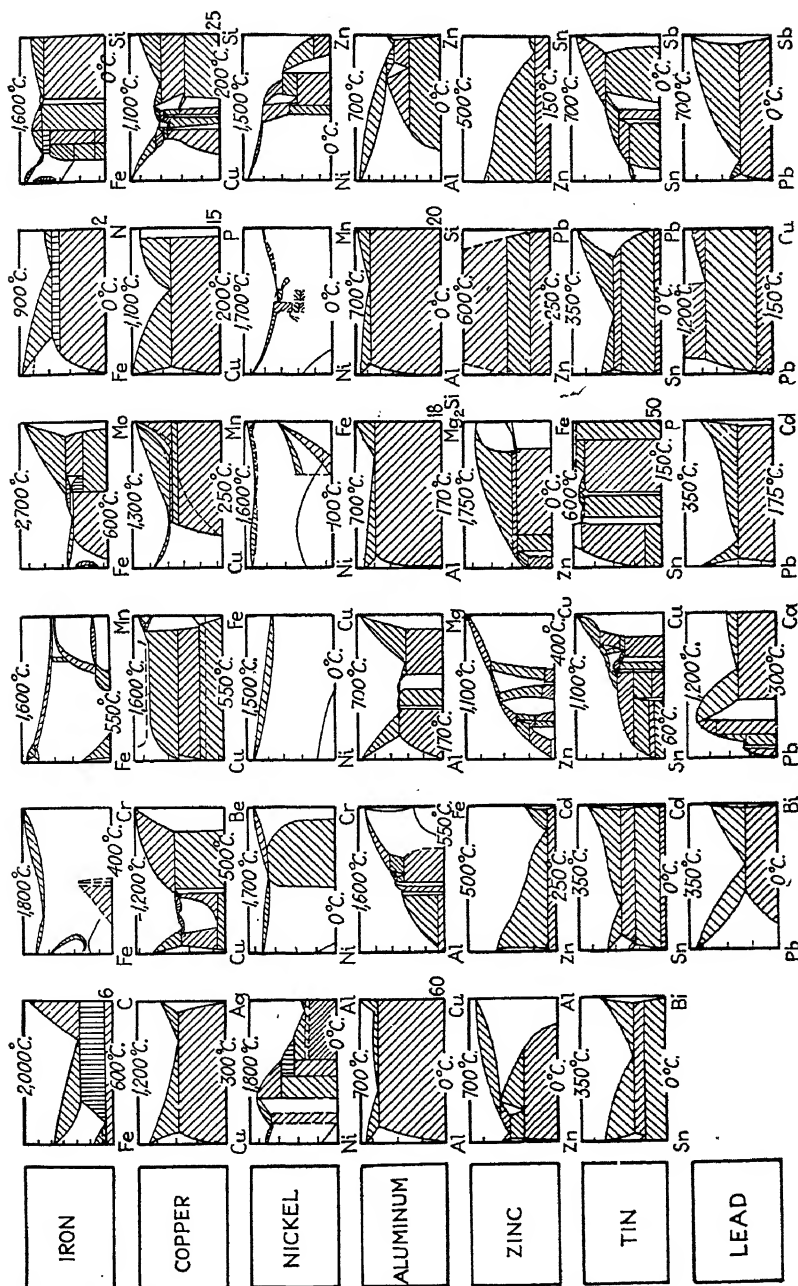
FIG. 256.—Constitutional diagrams of some industrially important binary alloys. (*From the later of International Critical Tables or Landolt Bornstein.*)

The periodic table (Table I, page 5) divides the metals into three general classes: (1) the high-melting heavy metals, (2) the low-melting heavy metals, and (3) the light metals. These metals generally form useful alloys within their own classification.

1. *High-melting Heavy Alloys.*—The first group of alloys, the high-melting heavy alloys, are extremely important. These metals, almost without exception, form alloys with each other—usually alloys with valuable physical properties. In most cases, they form solid solutions, particularly when more than two metals are present; silver is an outstanding exception. In this class there are five subgroups of metals that are especially important industrially. They do not include the metals chromium and manganese, which are more or less brittle, and others that are relatively too expensive and rare. The five subgroups are

a. The iron alloys, including cast iron, steel, and alloy steels.

b. The nickel alloys, similar to the iron alloys in physical properties, but more resistant to corrosion and also more costly.

c. The copper alloys, including brasses and bronzes, inferior to the previous two in strength and hardness, but chemically about as resistant as the nickel alloys. Their cost lies between the previous two and their extent of use, also midway. Alloys like monel metal, constantan, etc., are examples of the overlapping of the latter two groups, while nichrome shows the wide solubility for metals of other groups.

d. The silver alloys, more expensive than the three previous alloy groups. but demanded because of their beauty and chemical stability.

e. The noble-metal alloys with gold, platinum, palladium, iridium, etc., as the chief constituent. extremely expensive but necessary for certain purposes.

All these high-melting heavy alloys are capable of wide variation in alloying with each other. To them may be alloyed metals of other groups, such as silicon, carbon (steels and alloy steels), low-melting metals, such as zinc, tin, lead, and aluminum (brass, bronze, etc.). The possibilities of useful alloys in this series are by no means exhausted in the present day. Their excellent mechanical and chemical properties, which are the result of extensive solid solubility, make them extremely useful.

2. *Low-melting Heavy Alloys.*—The important metals of this group are zinc, cadmium, lead, bismuth, tin, and antimony, as

shown in tabular form on page 5. In the alloying of these metals with each other, solid solutions do not usually result or, at best, very limited solubility is present. Only two metals of this group form chemical compounds with other members: arsenic and antimony. The absence of such compounds (Guertler calls them *metallides* in harmony with chlorides, sulphides, etc.) leaves these alloys in the useful state, but their properties are those of the average between the two component metals, since they are simple aggregates of two kinds of crystals. All of them are of high specific gravity and low melting point, seldom over 400°C.

They can be alloyed to a certain degree with the high-melting metals, also for certain purposes with mercury, arsenic, aluminum, and the alkalies (Fig. 256). In industry, they are known as the *white metals*.

3. *The Light Metals.*—These are built up with either aluminum or magnesium as the base metal. The possible additions are

    a. Zinc and tin, unlimited in amount; silicon up to 15 per cent.

    b. Magnesium to 2 or 10 per cent; beryllium, rare earths, boron, carbon, silicon, titanium, vanadium, zirconium, chromium, molybdenum, tungsten, tantalum, thallium, manganese (up to 2 per cent), iron (up to 1 per cent), cobalt, nickel (up to 3 per cent), copper up to 8 per cent, tin, and antimony. All of these, only in small quantities, however.

    c. Alkalies and alkaline-earth metals; phosphorus, arsenic, sulphur, nickel, bismuth, lead, cadmium in not more than very small proportions and with other additions of greater amounts.

THE IRON ALLOYS

Steel

Because of its uncontested first rank of importance, steel—*i.e.*, the low-carbon part of the iron-carbon alloy system—has been used as an example to illustrate principles in many cases throughout the earlier parts of this text, and little is left to add to what has been developed previously, without entering the field of the monographs on steel. For example, the constitutional diagram of the iron-carbon alloys is given in Fig. 257 and Fig. 142, page 184. The process of solidification of a typical steel when cast, and the reverse of this process, when the same steel is heated in a furnace beginning at room temperature, are described

on pages 185 to 189. Typical microstructures of steels from 0.0 to 1.1 per cent carbon, when cooled slowly to room temperature, are given on page 186.

The quenching of steel is discussed from a fundamental standpoint on pages 219 to 221. The engineering aspects of the

FIG. 257.—The iron-carbon diagram. (*Metals Progress*, 1940 *Reference Issue*.)

heating and quenching of steel have had some notice on pages 309 to 317 in connection with furnaces and quenching media, as has also the matter of design of objects for heat-treatment.

Grain Size and Deep-hardening Quality.—One of the more recent developments in understanding the behavior of steel, particularly during heat-treatment, is the realization that the size of the austenite grains obtained upon heating into the γ range, in Fig. 257, above, determines to some extent how fast

the steel will transform on quenching.[1]   Thus, austenite that has a fine grain size, when it reaches the transformation temperature on cooling, with its relatively larger total area of grain boundaries, has a larger area of instability when the austenite is quenched, and therefore transforms quickly to soft pearlite.   Such a steel is said to be *shallow hardening*, because the surface layers only can be prevented from transforming to soft pearlite when the steel is quenched.   A coarse-grained austenite transforms much more slowly, and the deeper regions of the object can be retained in the martensitic condition.   Such steels are said to be *deep hardening*.[2]

Grain Size and Hardening Range.—Since the coarse-grained steels are those with grains that grow rapidly and at a relatively low temperature in the austenitic region, it follows that they must not be heated very far up into the austenite field or the grain size, after quenching, will be quite coarse.   They are often and quite properly said to be *inherently coarse grained*.   Depending on the properties desired, they must, therefore, be quenched from a temperature just above their upper critical point, to obtain a fine-grained steel, or to a slightly higher temperature to obtain a structure that will be coarsened.   The fine-grained steels, on the contrary, may be heated far up into the austenite field (as is done in case carburizing, for instance) without loss of grain refinement in the finished piece.   They may thus be called *inherently fine-grained* steels.   This means that the fine-grained steels have a broader range of hardening temperatures, which is a distinct commercial advantage.   Grossmann has pointed out that for each steel there is a minimum temperature below which coarsening will not take place, however long a time elapses.

Grain Size and Homogenization.—Another aspect of grain size with relation to depth of hardening is the incompleteness of diffusion of ferrite or Fe_3C from grain boundary to grain

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[1] Grain growth in the heating of a cold-worked metal is discussed in Chap. III.   When a new phase originates by polymorphic transformation on heating as described on page 40, the grain size of the new phase is usually larger, the higher the temperature to which it is heated and the longer the time it is held at that temperature.   Grain size changes but little during cooling down.

[2] See WILSON, R. L., "Grain Size in Steel," *Metal Progress*, August, 1934; BAIN, EDGAR C., *Trans., Am. Soc. Steel Treating*, **20** (5), November, 1932; UPTON, G. B., Cornell University, correspondence with the author; GROSSMANN, M. A., *Am. Soc. Metals*, **22** (10), 861, December, 1934.

center, in coarse-grained steels, when the steel is heated into the austenite field and held only a short time. Some regions of each grain will be higher in carbon than others, and, upon quenching, decomposition of all the austenite will take place more rapidly, owing to the earlier inception of nuclei of ferrite or Fe_3C in the more concentrated regions. Holding the steel for a long time in the austenite region permits the formation of homogeneous austenitic grains as the result of diffusion, and the austenite now has no regions of unequal concentration to promote breakdown. It is called *stabilized austenite*. The finer the austenitic grain size, the less distance ferrite or Fe_3C must diffuse to reach the center of the grain and thus to homogenize the composition.

High Holding Temperatures Promote Stability.—Furthermore, the rate of decomposition of austenite is decreased when the metal is held at a higher temperature prior to quenching. At higher temperature the austenite, particularly in tool steels, will take into solution more carbon, vanadium, tungsten, manganese, chromium, nickel, and other alloy elements; and, as a rule, the more concentrated austenites will break down less rapidly and therefore give a deeper hardening effect.

Determination of Grain Size.—The grains of steel at room temperature are formed from nuclei within the austenite grains, and consequently room-temperature grain size does not necessarily give any measure of the prior austenitic grain size. Since the rate of decomposition of austenite depends upon the austenitic grain size and not on the resultant room-temperature grain size, it is necessary, for heat-treating purposes, to obtain the grain size of the steel in the austenitic range. The consideration that the austenite grains exhibit a tendency to grow in size as the temperature is raised above the critical temperature makes it necessary to measure the austenite grain size at the temperature from which the piece is to be treated.

The McQuaid-Ehn Test for Grain Size.—The austenitic grain size of a steel is usually determined by the McQuaid-Ehn test, although a preference for other methods is growing rapidly. The steel is heated for 8 hr. in a solid carburizing compound to 1700°F., until a carburized zone of hypereutectoid (above 0.85 per cent C composition) 0.05 in. or more deep is obtained. Cooling is carried out slowly enough to obtain a pearlitic structure. The excess carbon (over 0.85 per cent) diffuses to the austenite grain bound-

aries and precipitates out as Fe_3C, forming envelopes of cementite around the austenite grains. The grain size is the average area within the envelopes of cementite grain boundaries, measured by counting the number of grains in 1 sq. in. of area at 100 magnifications. Thus, if a steel has one grain per square inch, its grain size is No. 1; two grains per square inch is No. 2; four grains per square inch is No. 3; and so on by geometric progression to No. 8 grain size, which has 128 or more grains per square inch. For practical purposes, Nos. 1 to 5 may be grouped as the coarse-grained steels,
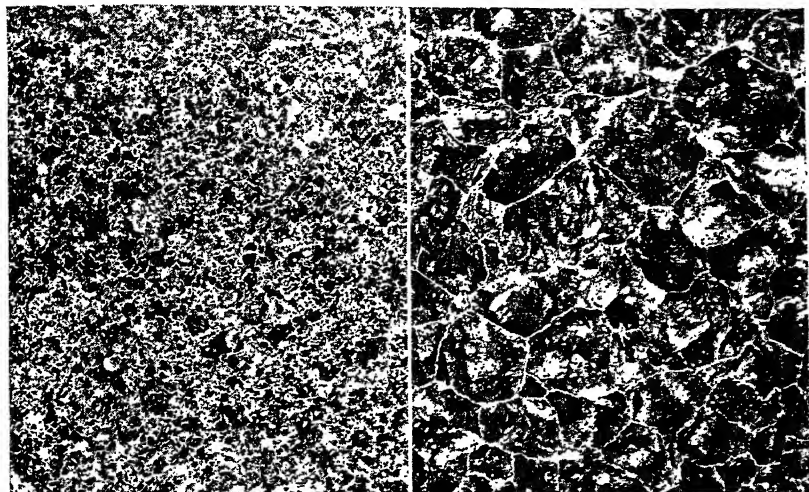
FIG. 258.—No. 8 grain size. (*McQuaid-Ehn.*) (*Courtesy of Timken Steel and Tube Company.*)

FIG. 259.—No. 3 grain size. (*McQuaid-Ehn.*) (*Courtesy of Timken Steel and Tube Company.*)

while Nos. 6 to 8 are fine-grained steels. Figures 258 and 259 show a coarse- and a fine-grained steel. When the cementite precipitate has coalesced at the grain boundaries and become encased in a wide ferrite layer, the steel is said to be *abnormal*. The fine-grained steels show this structure most frequently. The abnormally shallow hardening of these steels is now attributed to their fine grain size. Figure 260 shows various degrees of abnormality.

The major objection to the McQuaid-Ehn test is that it gives only the grain size at 1700°F., whereas the heat-treating temperature may be above or below that temperature and exhibit an entirely different grain size at the heat-treating temperature.

The most promising of the recent methods for austenitic grain size determination involves the quenching of small steel bars from the temperature at which the steel is to be treated, at a rate
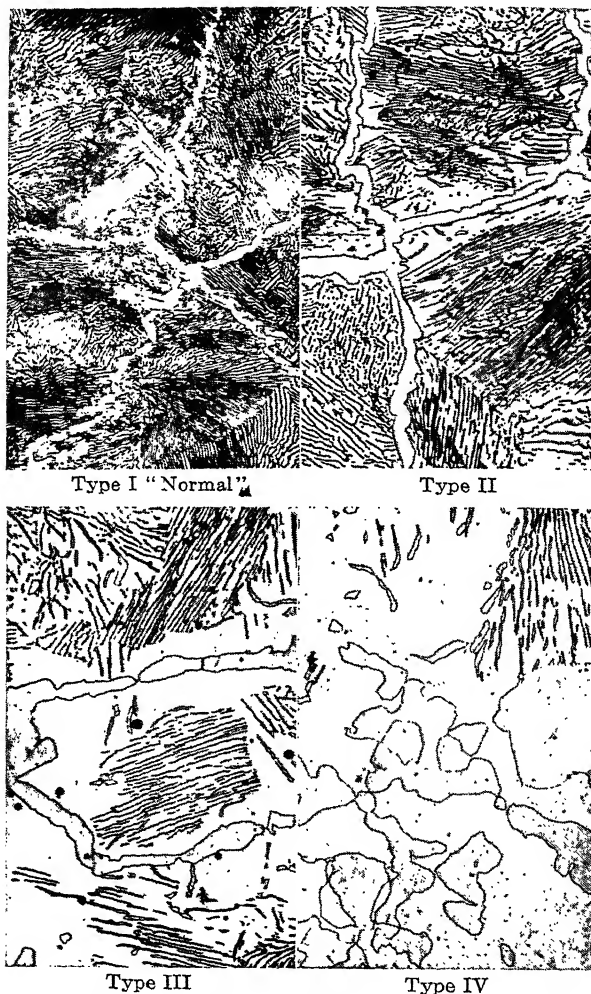
FIG. 260.—Degrees of abnormality in hypereutectoid steel. $\times$ 1,000.   (*Courtesy of United States Steel Corporation Research Laboratories.*)

just slightly slower than the critical cooling rate (the critical cooling rate is that necessary to transform the piece entirely to martensite, see page 226), so that a slight amount of transforma-

tion will take place. Naturally the first transformation takes place at the unstable grain boundaries, and consequently the austenite grains are surrounded by a low-temperature decomposition product. This rate of cooling is obtained by a differential quench, in which one end of the specimen is quenched rapidly and the other is not. A range of cooling rates results from above the critical rate to below that rate. The specimen is then sectioned until the cross section is obtained in which the cooling took place at the proper rate.

Control of Grain Size.—Fine grain size seems to result when steel is treated in the ladle with strong deoxidizers, such as aluminum, after a previous deoxidation with silicon or manganese. Possibly the particles of alumina act as abundant nuclei for the development of austenite grains, or they may obstruct grain growth in the austenite.

Properties versus Grain Size.—Aside from the question of hardenability, the grain size of steel is important in several respects. Coarse-grained steel machines more readily, thus lowering the cost of the machining operations. However, the finish produced by machining fine-grained steel is said to be smoother also. When annealed, coarse-grained steels are more likely to possess a lamellar pearlite structure of fairly low hardness. This structure machines well:

The coarse-grained steels forge more easily, *i.e.*, with less power application, but if sufficient power is expended on the fine-grained steels, their superior tenacity enables them to undergo large deformation without rupture. If heated to a temperature so high that it coarsens, the fine-grained steel will naturally behave like a coarse-grained steel.

Above 900° to 950°F. the coarse-grained steels have greater "creep" resistance. Below these temperatures, the fine-grained steels are superior in this respect. In general, Wilson observes that the coarse-grained steels are recommended for good machinability, intense hardening, easy coarsening of structure, and high-temperature service above 950°F. (as in oil refineries). The fine-grained steels are recommended for economical casehardening, good toughness, superficial hardening of the directhardening type, small warpage in hardening, best mechanical properties of untreated steel, and high-temperature service below 950°F. (as in steam power plants). It seems probable

that the ancient term *body* for quality steels is explained largely by grain size and partly by aging behavior (*q.v.*).

Cast Iron

The commercial iron-carbon alloys containing from 1.7 to 4.5 per cent carbon, as shown in Fig. 257, are called *cast iron*. These alloys will normally contain some eutectic of austenite-cementite,
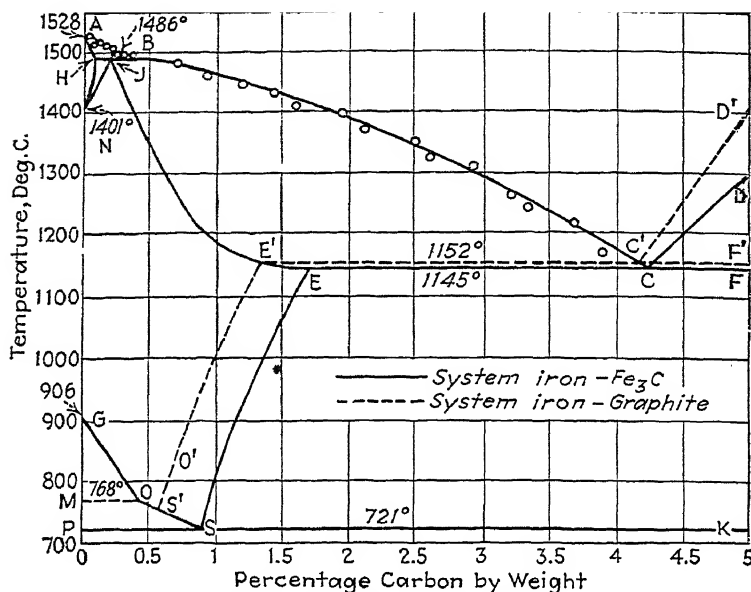
FIG. 261.—The system iron-carbon.

whereas the steels, lying below 1.7 per cent carbon, will contain no eutectic.

Rapidly Cooled Alloys—White Irons.—When a cast iron is cooled rapidly from the liquid state, the structures that result are exactly what one would expect in the system Fe-Fe$_3$C—namely, to the left of the point *C* (Fig. 261) primary grains of austenite (cored, *i.e.*, higher in iron at the cores and progressively richer in carbon toward the boundaries), surrounded by a eutectic of austenite and cementite (called *Ledeburite*), separating at the temperature of the line *ECF*. At lower temperatures the austenite, both the primary and that in the eutectic, will precipitate a little Fe$_3$C and then at 730°C. undergo the

eutectoid reaction to ferrite and cementite, the structure called
pearlite. Figure 262 shows the structure of the alloys from
1.7 per cent carbon up to 4.5 per cent carbon. It will be noticed
that the proportion of primary austenite grains (black) is 100 per
cent at 1.7 per cent carbon (no eutectic) and decreases gradually
to 0 per cent at 4.2 per cent carbon, being replaced there by
100 per cent eutectic. In commercial cast irons the eutectic
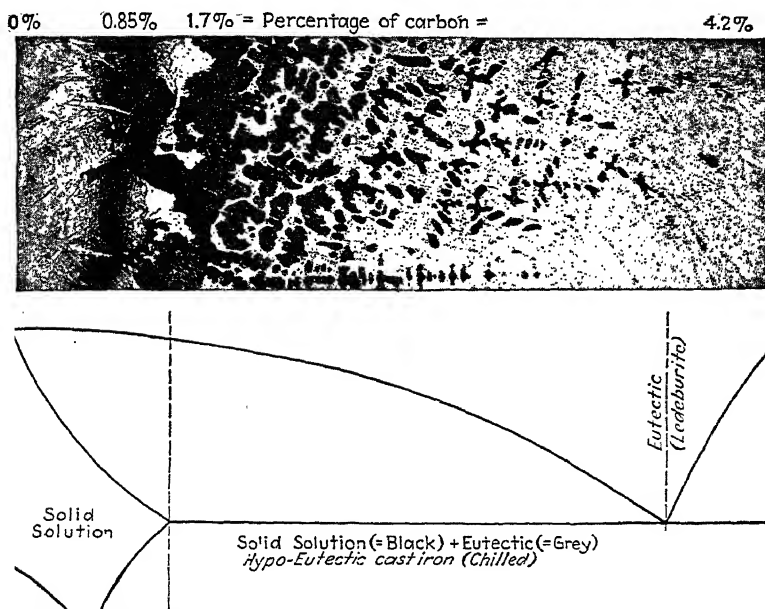
FIG. 262.—Change in microstructure of cast irons as the carbon content increases.
(*W. P. Sykes.*)

point may lie between the normal 4.2 per cent C down to 2.5 per
cent C, owing to the effect of alloying agents. Si, in particular,
moves the eutectic and eutectoid points far to the left.

To the right of the 4.2 per cent point, the rapidly cooled
alloys precipitate primary cementite crystals along the liquidus
line *CD* (Fig. 261). These crystals appear as white needles in Fig.
263, and these are surrounded by the same austenite-cementite
eutectic that is mentioned above. At lower temperature, if
equilibrium reigned, the austenite in this eutectic likewise would
break down by the eutectoid reaction to ferrite and cementite.

Thus the case for rapidly cooled alloys of these compositions
seems quite simple. It should be pointed out clearly, however, at

this point that Fe_3C is an unstable phase in these alloys. For this reason the curve CD for the separation of the Fe_3C phase must lie *below* the curve $C'D'$ for the separation of the more stable phase—graphitic carbon. Apparently the rate of nucleus formation of Fe_3C increases much more rapidly with increased supercooling than does that of graphite, so that rapid cooling leads to the formation of Fe_3C crystals only. These alloys are called *white cast irons*. They are glass hard and brittle, but
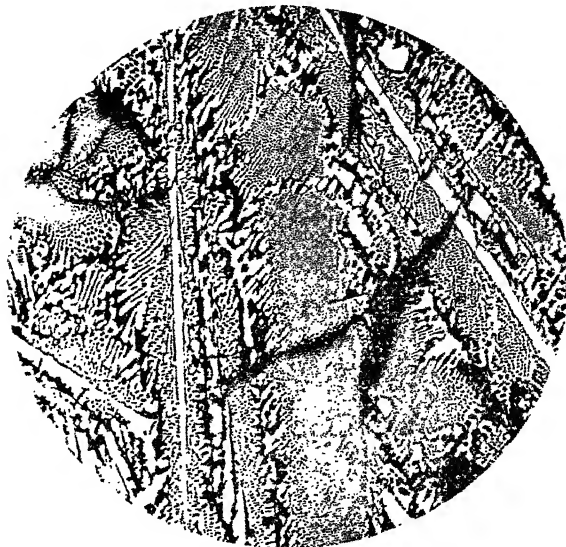
FIG. 263.—Hypereutectic cast iron. The white needles are primary Fe_3C. The background is eutectic austenite Fe_3C. (*Oberhoffer.*)

the hypoeutectic white cast irons have many uses. Because of their hardness, these alloys are desired at the surfaces of rolls for rolling steel ingots into shapes such as bars and rails. The outside of the roll is given such a surface by inserting into the mold, where the roll is to be cast, a metal lining, called a *chill*. When the liquid cast iron touches these chills, it cools rapidly and forms a layer of "white iron" all around the surface of the roll, while the interior of the roll is not chilled. A similar treatment is provided in the casting of chilled car wheels, to harden the treads.

Slowly Cooled Alloys—Gray Irons.—When cooled slowly, the hypoeutectic alloys (up to 4.2 per cent carbon) precipitate

austenite as before, but at the temperature $E'C'F'$ (Fig. 261) the liquid tends to form a *graphite eutectic* instead of an Fe_3C eutectic.
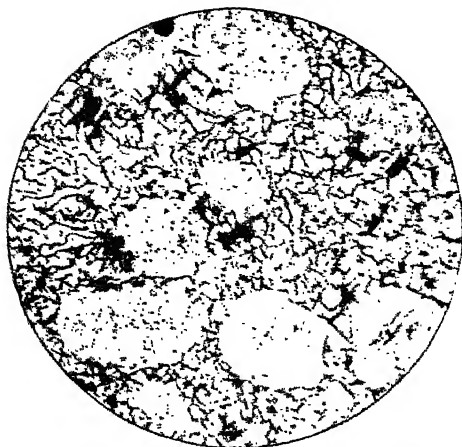
Fig. 264.—Austenite grains (white) surrounded by graphite-austenite eutectic in a hypoeutectic cast iron.   Unetched. $\times$ 350.   (*Geiger.*)

Fig. 265.—"Kish" (black bars) and graphite eutectic in a slowly cooled 7 per cent carbon iron.   Unetched. $\times$ 20.   (*Oberhoffer.*)

Figure 264 shows the graphite eutectic in such a cast iron.   The large light areas are primary austenite grains (which later may

have broken down into pearlite, but when unetched these areas appear homogeneous). Likewise, the light background of the

FIG. 266.—"Mottled iron" graphite (black) surrounded by ferrite (white) originally combined as Fe_3C.   × 350.   Total C, 3.31 per cent; graphite, 2.81 per cent; silicon, 1.93 per cent.   (*Geiger.*)

FIG. 267.—Pearlitic cast iron. P = pearlite; L = ledeburite.   × 900.   (*Heyn.*)

eutectic is austenite or its decomposition product, pearlite, unetched.

To the right of 4.2 per cent carbon point, the slowly cooled alloys precipitate primary graphite (called *kish*) along the line $C'D'$ (Fig. 261) until the liquid reaches the composition C', when the graphite eutectic separates. The structure of such an alloy is shown in Fig. 265.

Intermediate Cooling Rates. Reheating—Mottled Irons.—If the cast irons are cooled at intermediate rates, both Fe_3C and graphite will appear in the structure. No doubt a part of the graphite is formed directly from the liquid and a part by the decomposition of Fe_3C. Such cast irons are called *mottled irons*. A similar structure may be obtained by reheating a white iron. The Fe_3C decomposes partly or wholly to graphite. Figure 266 shows two black streaks of graphite surrounded by ferrite. Originally this graphite and ferrite were combined as Fe_3C. In other cases the Fe_3C will have decomposed at a temperature where the iron liberated is in the γ form and can dissolve 0.85 per cent or more of carbon to form austenite. In this case the graphite will be surrounded by pearlite instead of ferrite at room temperature, as shown in Fig. 267. The so-called *pearlitic cast irons* are of this type.

The Useful Properties of Cast Iron.—Cast iron, as a result of its high-carbon content, has a low melting point (1150° to 1350°C.) as compared with steel (1500°C.). The melting of cast iron in the cupola is, therefore, a relatively simple matter. It is cheap, having avoided the costly refining in the open hearth that is needed to make steel. Its fluidity is greater (particularly if phosphorus is high) than that of steel and its viscosity apparently is less, thus permitting it to flow quickly and completely into the sharp angles, or narrow passages of an intricate mold. The separation of graphite during freezing contributes an expansion in volume that offsets a part of the tendency to shrinkage cracking when the metal cools and also helps to force the pasty metal yet more sharply into the angles of the mold. Dr. J. T. Mac-Kenzie has pointed out, however, that the separation of graphite during freezing is just about as much of a nuisance as a help, especially in large sections. The first layer of metal to freeze expands due to the formation of graphite, thus causing a volume too large to be filled by the still liquid metal. As the second layer freezes it wants to expand, thus holding the original large

volume. If the expansion of the last metal to freeze is great enough, you may still obtain a sound casting. However, ordinarily it does not quite make it, so that you have a shrink.

The graphite, being present usually in flakes, lowers the tensile strength of the iron almost as much as complete discontinuities or cracks in the metal would do. While the tensile strength of cast iron is low, its compressive strength is much better. But the graphite also confers machinability. It acts as a carrier for oil, thus giving cast iron most of its wear resistance, and freedom from galling. It allows the material to "breathe" under alternating heating and cooling and it is responsible for the very high damping capacity of the material, which is after all one of its most valuable properties. In cast-iron vessels for chemical use the graphite remains in place, tends to prevent contact of the corrosive reagent and the metal itself. Frequently a cast-iron vessel will outlast the same thickness of steel by several times solely due to this graphitic residue, though in many cases an ordinary corrosion test with the graphite continually removed would show a faster rate of attack on the cast iron than on the steel.

Malleable Cast Iron.—In 1722 Réaumur invented a process for treating a white-cast-iron object by heating it, packed in iron oxide, to some 625° to 875°C., for about 120 hr. Thin castings (usually under $\frac{1}{2}$ in. thick) when so treated will lose practically all of their carbon (by diffusion of oxygen into the iron and of CO or CO_2 out of it). They are called *white-heart* malleable castings, because even the core or heart of the object is white, being free of carbon. In America the practice is to chill the casting so that it will be either entirely white (no graphite) or else black only at a small area at the center of a piece 1 in. thick (*black heart*). The castings are now heated to the above-mentioned temperatures for about 60 hr. instead of 120 hr. Graphite precipitates from the Fe_3C, not however in the form of flakes, but in a finely comminuted condition, to which the name *temper carbon* has been given. In this form it is not nearly so weakening to the casting as flakes of graphite would be.[1]

Figure 268 shows the structure of *black-heart* malleable cast iron. Malleable cast iron has physical properties between those of gray iron and those of steel. Tensile strength is 50,000 to

[1] Professor Stoughton has likened it to finely ground mica in a matrix of putty, as compared with flake mica in the same putty.

60,000 lb. per square inch; elongation, 10 to 15 per cent in 2 in.; reduction of area, 5 to 12 per cent.

Growth of Cast Iron.—An interesting phenomenon in certain cast irons, which limits their use in high-temperature service, is
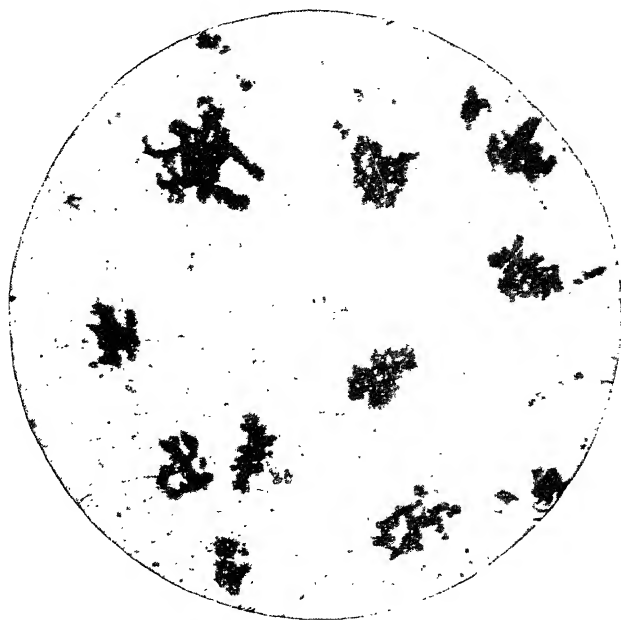
FIG. 268.—Malleable cast iron. Temper carbon (black) in ferrite (white) × 200. (*Roy M. Allen.*)

the occurrence of a growth in volume. Under certain conditions of heat-treatment in oxidizing atmospheres, some cast irons may be made to grow as much as 50 per cent in volume, although the growth normally encountered is much less, a normal maximum being in the range of 10 per cent. The growth is generally caused by two factors: (1) The rather open structure resulting from the combination of graphite and iron is especially susceptible to internal oxidation along continuous fissures opened up along the graphite plates during heating, and the resulting metal oxides occupy a greater volume than the metals from which they were formed, causing growth. (2) Graphite, which is formed by conversion of combined carbon, occupies a greater volume than the combined carbon and causes growth. The temperature for easy growth must at least be above 550°C.

By the proper choice of composition and by proper heat-treatment of cast irons, growth may be almost entirely eliminated. Alloying elements that tend to stabilize the carbides and increase the corrosion resistance of the matrix metal greatly reduce growth. Lowering the carbon content to about 2.50 per cent, along with a heat-treatment to assure the precipitation of all excess carbide as graphite, further reduces the growth possibilities to almost zero.

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THE COPPER ALLOYS
THE BRASSES

The copper-zinc alloys, or brasses, are the most important of the many copper alloys. The constitutional diagram is given in Fig. 269. The alloys may be divided into two simple groups.

1. The *alpha brasses* contain up to 36 per cent zinc and are simply solid solutions of zinc in the copper lattice. These alloys are sometimes given trade names such as *common high brass* (66 per cent copper, 34 zinc), *low brass* (80 per cent copper, 20 zinc), and *rich low brass* (85 per cent copper, 15 zinc). They may be worked both hot and cold and frequently are subjected cold to the more severe operations of cold heading, cupping, forming, and spinning.

The alloys in the alpha field solidify, as does a completely soluble alloy of the type described on page 162. The cast struc-
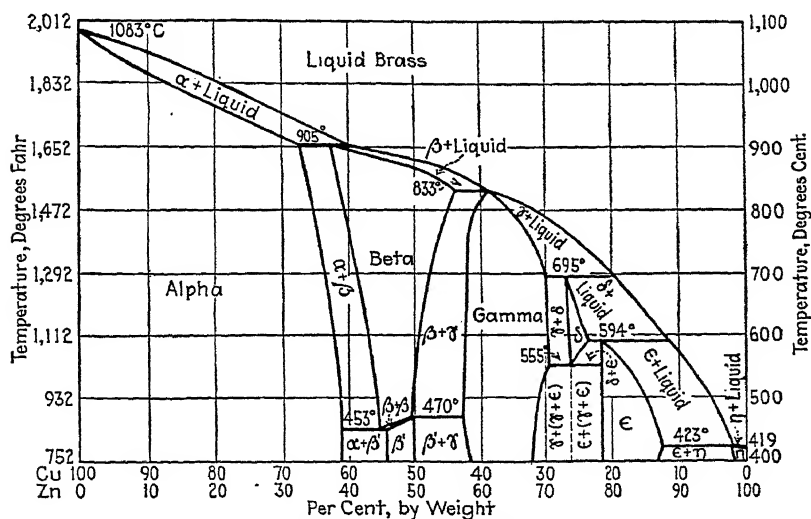
Fɪɢ. 269.—The constitution of the copper-zinc alloys. (*A. Phillips.*)

ture shows cored grains, similar to those shown in Fig. 121, page 164. The central cores are richer in copper than the subsequent layers. Annealing, or, more usually, working and annealing, causes these cores to disappear and results in a homogeneous single-phase structure such as that in Fig. 270*a*. (The stripes are due to twinning following annealing, the so-called *annealing twins*.)

2. The *alpha-beta brasses*, as their name indicates, are composed of two constituents. The most common alloy of this group is "Muntz metal" (60 per cent copper, 40 zinc). The microstructure in Fig. 270*b* shows the precipitate of α (white) solid solution from the β (black) upon fall in temperature. Its

similarity to the structure of Fig. 145, page 187, is obvious and it forms in the same way. At some 450°C. the β, which is an ordinary solid solution of zinc and copper atoms, with statistically random arrangement in the lattice, takes on a regular distribu-
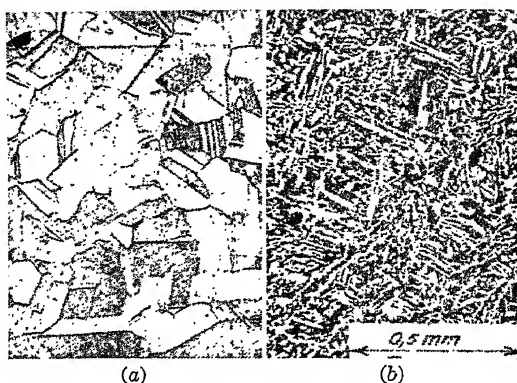
FIG. 270.—(a) Alpha brass showing twins; (b) alpha grains (white) precipitated in beta (black) "Muntz metal."

tion, and a superlattice, such as is noted on page 205 results. Heating these alloys to a high temperature, as Fig. 269 shows, will convert them into a homogeneous β solid solution, the α going back into solution at the higher temperature. Upon
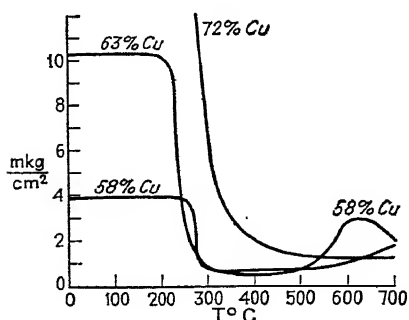
FIG. 271.—Notch toughness of three brasses at elevated temperatures. (*Sauerwald and Wieland.*)

cooling from the liquid state, certain alloys will form beta by a peritectic reaction, but most of the β forms by direct crystallization from the melt. The γ constituent is quite brittle and probably is the compound CuSn and its solutions.

Properties of the Brasses.— In melting, casting, and welding the brasses, special precautions are necessary to prevent evaporation of the zinc. In welding, silicon is used in the welding rod to retain the zinc. The silicon seems to form a film of SiO_2 over the liquid metal and so retain the zinc. Phosphorus is used to deoxidize the melt, but little or none is left in the metal when solidified. The casting properties are superior to those of copper.

The working of brasses that contain β grains must be done hot to avoid breakage. The α brasses are usually worked cold because of the weakness at temperatures above 300°C., as shown in Fig. 271. The plasticity improves again above 900°C. If α is present in a brass which at room temperature is α plus β, it must be worked at a temperature so high that all α has gone into solution in the α according to the diagram before the working begins.

The α brasses are progressively stronger, harder, and cheaper as the zinc content increases, up to some 35 per cent. The ductility increases up to 20 per cent zinc, then falls. The conductivity falls rapidly as the zinc content rises. The resistance to corrosion in general may be inferred from the electrochemical potential, which remains practically unchanged in the α range and rises only slightly in the field α plus β. Under some circumstances the corrosion resistance of brass is superior to that of copper.

Effects of Third Metals.—Lead above 0.25 per cent improves the machinability of brass but decreases the formability. Iron decreases the grain size and increases the tensile strength. Other elements may be added, as deoxidizers or to enter into solid solution in the α and strengthen it further, such as manganese and aluminum. An increased corrosion resistance usually follows, especially with aluminum, silicon, and nickel. Phosphorus improves the casting and surface properties.

Copper Alloys That Age-harden

Of the many copper alloys that age-harden, only one will be described, namely, copper-beryllium, the constitutional diagram of which is given in Fig. 272. The decreasing solubility of copper for beryllium with decreasing temperature is the most important feature. The decomposition of the β solid solution of 6 per cent Be content into a eutectoid of α and γ at 578°C. is important also. The γ constituent is very brittle and therefore of little use.[1]

Figure 273 shows the surprisingly great increase in strength of a 2 per cent beryllium alloy when quenched from 800°C., and annealing at temperatures between 250° and 350°C. Figure 274 shows the increase in strength when the untreated metal is drawn

[1] "Beryllium," p. 108, translated by Richard Rimbach and A. J. Michel, Reinhold Publishing Corporation, New York, 1929 (1932).

into wire, the increase upon heat-treatment, and the rise in conductivity upon heat-treatment. The combination of hard-
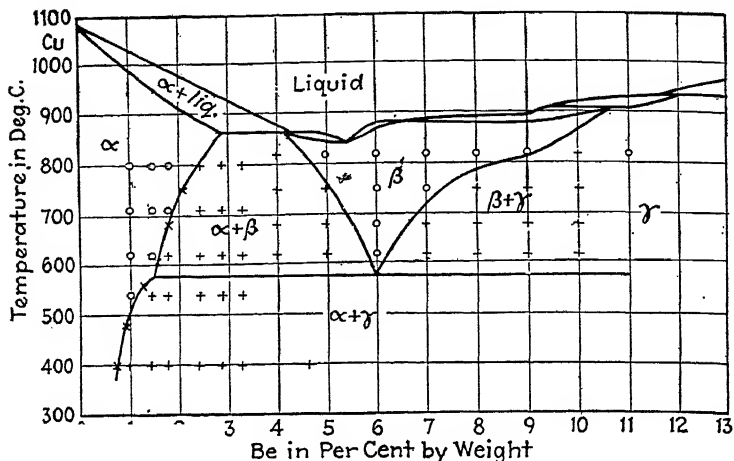
FIG. 272.—Constitutional diagram of the copper-beryllium alloys.
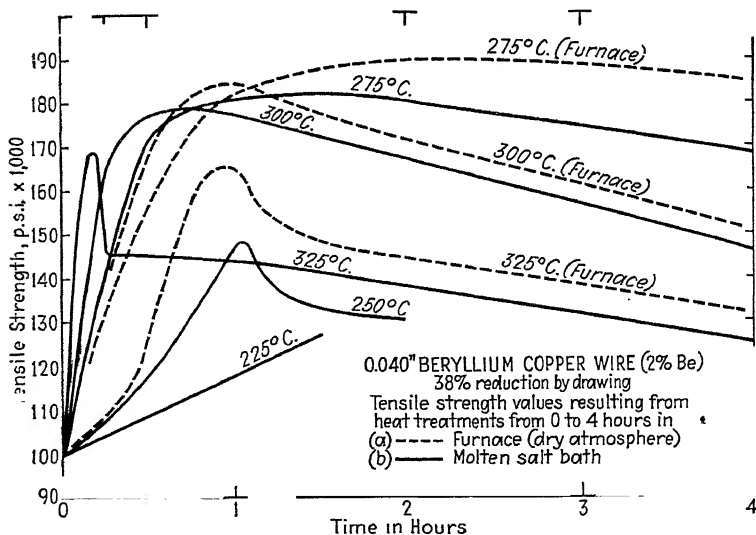
FIG. 273.—The effects of various heat-treatments on the tensile strength of beryllium copper. (*From the American Brass Company, "Anaconda Beryllium Copper."*)

ness and conductivity makes these alloys useful as springs for dynamo brushes.   The alloy of 97 per cent copper is hard enough to cut steel.   When made into a chisel, this "hard copper" will

cut steel. Other Cu alloys which exhibit commercially utilized age-hardening properties are CuNiSi alloys, CuNiAl alloys, CuSi alloys, and CuSiMn alloys. For a discussion of age hardening see page 229.
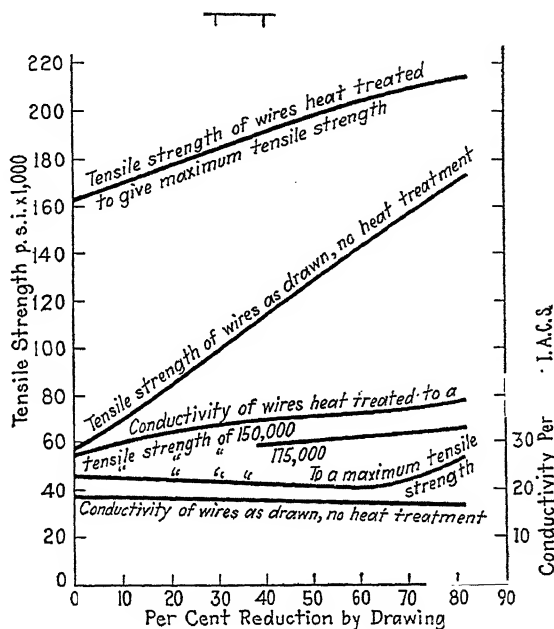
FIG. 274.—Tensile strength and conductivity of 2 per cent beryllium copper after heat-treatments and cold drawings. (*American Brass Company.*)

THE BRONZES

The simplest bronzes are the copper-tin alloys. Up to some 13 per cent tin, a solid solution in copper is formed, as shown at the left in Fig. 275. If the melt is chilled rapidly, some peritectic may form, even with alloys as low as 5 per cent tin, but usually not below 9 per cent. The compounds Cu_4Sn and Cu_3Sn are very hard and brittle. Figure 276 shows the α-Cu_4Sn eutectoid in a 15 per cent tin alloy.

The specific volumes of the liquid and solid copper-tin alloys are given in Fig. 185, page 240.

In melting the bronzes, oxidation of tin should be guarded against, as the oxide does not float out readily but forms films at the grain boundaries and destroys the metallic properties.
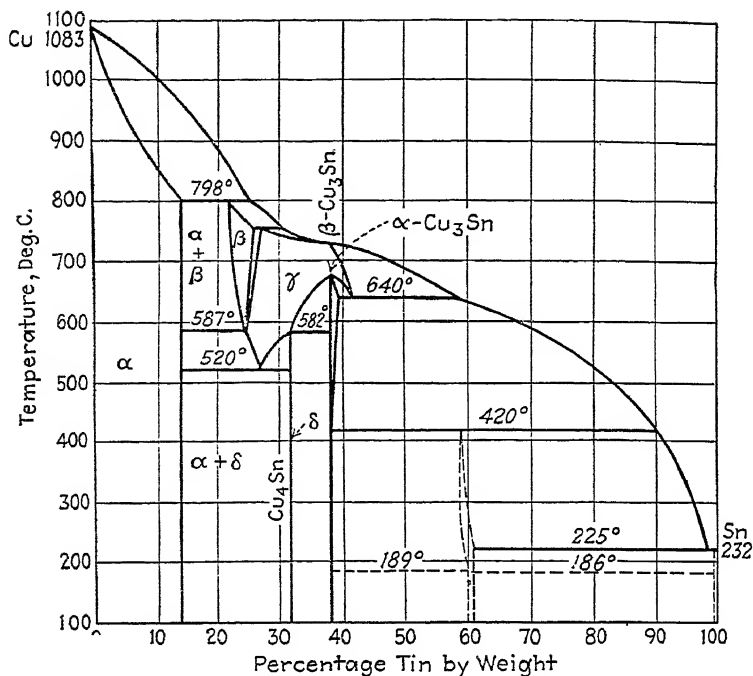
Fig. 275.—Constitution of the copper-tin alloys.   (*Bauer and Vollenbruck.*)
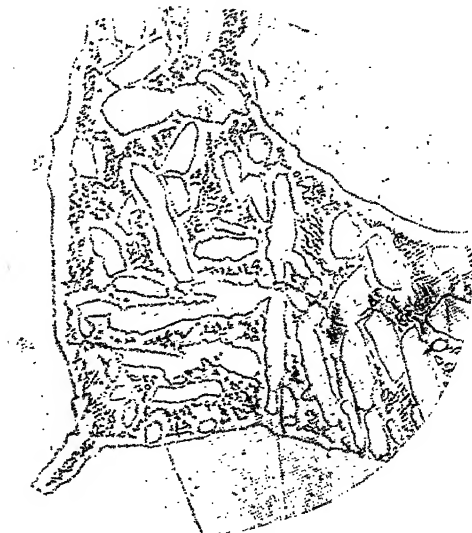
Fig. 276.—Copper-tin alloy with 15 per cent tin.   Primary alpha with alpha-Cu_4Sn eutectoid.   × 200.   (*Bauer and Vollenbruck.*)

The α bronzes are usually worked cold, although forging and pressing may be done at 650° to 700°C. Alloys with more than 10 per cent tin are usually cast only.

Effects of Third Metals.—Zinc up to 0.5 per cent acts as a deoxidizer and produces better castings, much as does phosphorus. Above 2 per cent zinc causes a decrease of strength. Lead is added to bronzes in small percentages to improve machinability. It is added to as high as 30 per cent for use in bearing metals because of the antifriction properties imparted. Iron imparts hardness and is sometimes used in machinery bronze. Arsenic, antimony, and sulphur impart brittleness and should be kept well below 0.1 per cent. Coinage bronze contains preferably 4 per cent tin, 1 per cent zinc. Gun metal contains preferably 10 per cent tin, 2 per cent zinc.

There is a very large and constantly growing list of alloys in which one or more metals are alloyed in small proportion with copper. Alloys of aluminum, manganese, silicon, nickel, magnesium, phosphorus, and countless others have been marketed, frequently under copyrighted names. In this group are Olympic Bronze (96 per cent Cu, 3 Si, 1 Zn) and Everdur (96 per cent Cu, 3 Si, 1 Mn). Discussion of them will be omitted, not because they lack commercial importance but because such discussion does not fall within the scope of this text.

Copper-Silver and Copper-Gold

These alloys include sterling silver (92.5 per cent Ag, 7.5 Cu) and the gold alloys (24 carats = pure gold, 18 carats = 18/24 = 75 per cent gold, 25 copper; etc.). They are of considerable commercial importance, but involve no new basic principle.

Selected Literature

"National Metals Handbook," American Society for Metals, Cleveland, 1939.

Hoyt: "Metallography," vol. II, McGraw-Hill Book Company, Inc., New York, 1921.

Genders and Bailey: "The Casting of Brass Ingots," 190 pp., British Non-Ferrous Metals Research Association, 1934.

THE ALUMINUM ALLOYS

Age-hardenable Alloys

Only the most important and, of these, the most typical commercial alloys of aluminum will be mentioned here. Without

question, the most interesting are the age-hardenable alloys. The behavior of the Al-Cu alloys described on pages 229 to 232 may be considered sufficiently typical, although each of the many age-hardenable aluminum alloys possesses individual peculiarities. The Al-Cu equilibrium diagram is shown in Fig. 277. The important solution zone is shown enlarged. Other important age-hardening alloys of aluminum include aluminum-lithium, aluminum-zinc, aluminum-copper-manganese-silicon, aluminum-
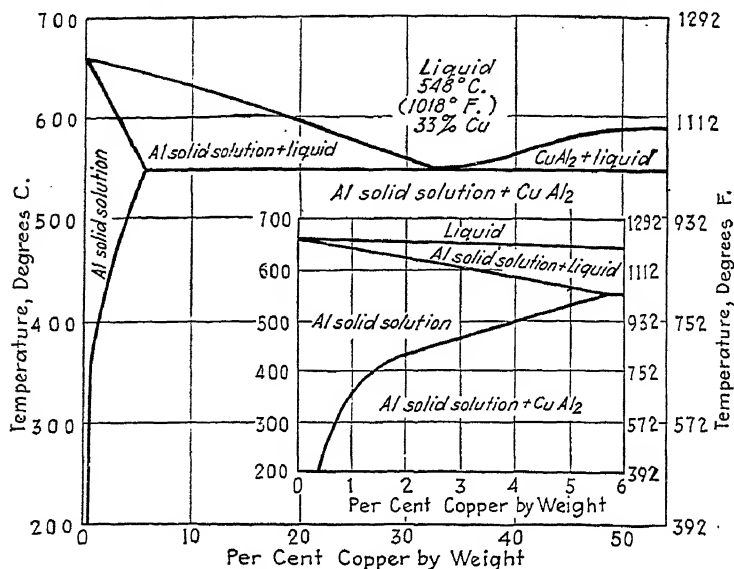
Fig. 277.—Constitution of the copper-aluminum alloys.

magnesium-silicon, aluminum-copper-magnesium-silicon-manganese, and many others. They will not be described individually in this text.

CASTING ALLOYS

Aluminum Silicon. Modifying.—Of the cast aluminum alloys, perhaps the Al-Si series, which was used to illustrate the simple eutectic reaction on page 157, is most interesting. The constitutional diagram of the Al-Si alloys is fully explained in that connection and a representative set of microstructures is shown. The 5 per cent silicon alloy casts well and resists corrosion, owing to the formation of a protective film of $SiO_2 \cdot xH_2O$ as noted on page 264. It is relatively high in fluidity and free from hot-

shortness. It is suitable for thin sections and for those which must be pressuretight. The 10 per cent alloy has somewhat better fluidity. The 13 per cent alloy is usually treated by a process called *modifying*. If 0.05 per cent of metallic sodium is added to a melt of 13 per cent silicon alloy, usually by placing

Fig. 278a.—A normal 14 per cent silicon-aluminum alloy. × 100. (*Courtesy of L. W. Kempf.*)
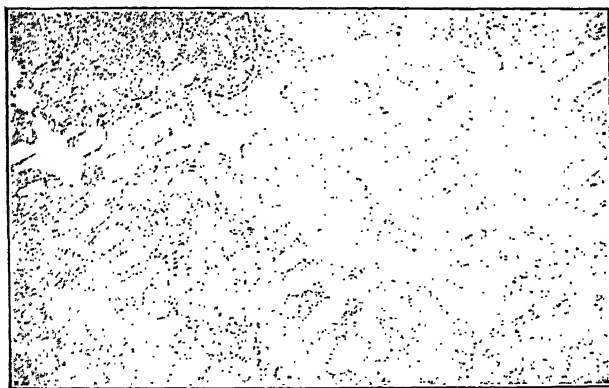
Fig. 278b.—A "modified" 14 per cent silicon-aluminum alloy. × 100. (*Courtesy of R. S. Archer.*)

the sodium in an empty crucible and pouring the metal upon it, the structure of the eutectic is greatly refined and the physical properties of the alloy are improved, the tensile strength of a normal alloy rising from 20,000 to 27,000 lb. per square inch and the elongation rising from 3 up to 12 per cent. The structure of a normal and a modified alloy is given in Fig. 278. Apparently

the sodium depresses the rate of crystallization of silicon (but not the rate of nucleus formation), causing the eutectic to appear nearer the silicon side and at a lower temperature, as shown in Fig. 279.   For modifying see also page 37.
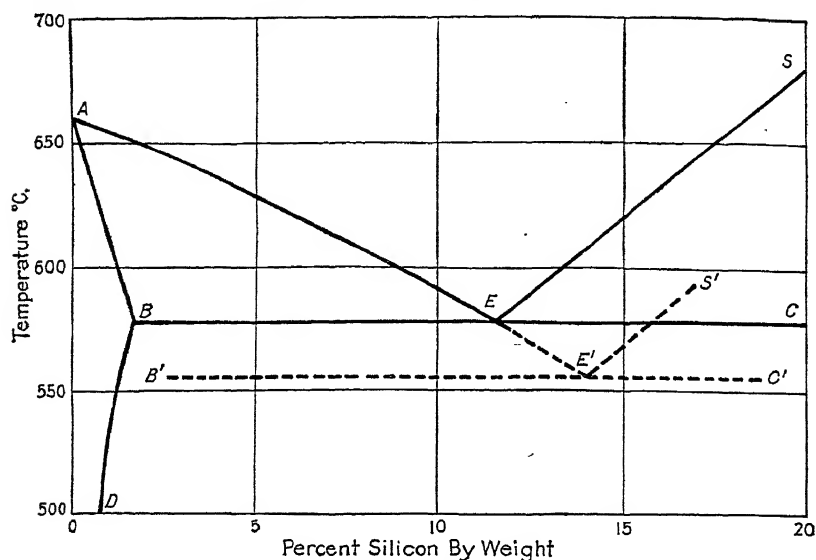
Fig. 279.—Constitution of the silicon-aluminum alloys showing the metastable equilibrium caused by modifiers.   (*Courtesy of R. S. Archer.*)

The aluminum-copper alloy containing 4, 8, or 12 per cent copper is a widely used casting alloy in America as is also the Al-Zn alloy in England.   Figure 256, on page 341, shows the general features of both of these alloy systems.

Selected Literature

EDWARDS, FRARY, and JEFFRIES: "The Aluminum Industry," 2 vols., McGraw-Hill Book Company, Inc., New York, 1930.

BUDGEN, N. F.: "The Heat Treatment and Annealing of Aluminum and Its Alloys," Chapman & Hall, Ltd., London, 1932.

FUSS, V.: "Metallographie des Aluminiums und seiner Legierungen." Verlag Julius Springer, Berlin, 1934.

NICKEL AND ITS ALLOYS

Nickel forms a solid solution with iron as is shown in Fig. 256, page 341.   Thus, in steel and cast iron, nickel is usually found in the ferrite phase, which it makes stronger, tougher, and usually finer in grain size.   Iron with 26 per cent nickel forms an alloy,

the thermal expansivity of which is nearly zero. This alloy is called *Invar* and is used for tape measures and watch parts, and in automotive pistons. The 80 per cent nickel alloy is called *permalloy*. It has a very high magnetic permeability at low field strengths. *Hipernik* is a 50 per cent nickel alloy of somewhat similar properties. It is used for the cores of current and of audiofrequency transformers.
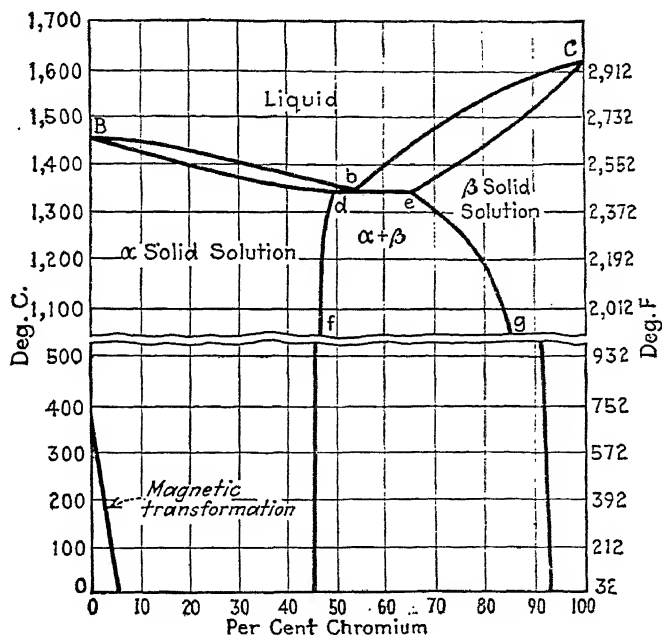
Fig. 280.—Constitution of the nickel-chromium alloys. (*National Metals Handbook.*)

With chromium and iron, nickel makes up the type of stainless steel called "18 and 8," *i.e.*, 18 per cent chromium, 8 per cent nickel. The iron-nickel-chromium and nickel-chromium alloys are frequently used for their heat-resisting qualities and as resistor elements in electrical heating. The nickel-chromium diagram is given in Fig. 280.

All the copper-nickel alloys, including monel metal (67 per cent Ni, 28 Cu, 2 Fe), are homogeneous solid solutions in the equilibrium condition. The diagram is given on page 161 and a typical microstructure on page 164. They are ductile, malleable,

and resistant to corrosion.   German silver is a copper-nickel-zinc alloy.   It contains no silver.

Precipitation-hardening Ni alloys are obtained by alloying Ni with Cu and Si, Al, or Be.   The most important of these at present is *k* Monel, of composition 66 per cent Ni, 29 per cent Cu, 2.75 per cent Al.

Selected Literature

Nickel and Its Alloys, *Bur. Standards, Circ.* 11, 1924.

CAMPBELL, W.: A List of Alloys, *Proc. Am. Soc. Testing Materials*, 1930.

HOYT: "Metallography," vol. II, McGraw-Hill Book Company, Inc., New York, 1921.

"National Metals Handbook," American Society for Metals, Cleveland, 1939.

TIN

Tin[1] is used largely as a coating on iron but also with lead in solders, with antimony and some other metal in type metals,
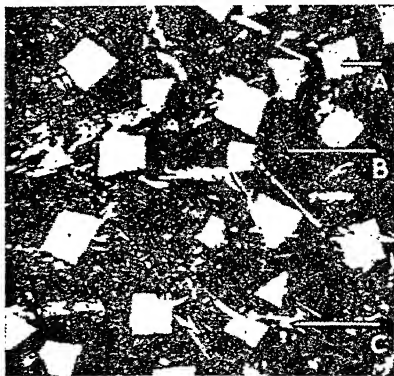
FIG. 281.—Babbitt metal.   × 150.

Britannia metal, and in babbitt for lining bearings.   The antimony content is usually kept below 25 per cent to avoid brittleness.

With bismuth and other metals, tin forms the fusible alloys used in fire-sprinkling systems and trick spoons (Wood's metal, 50 per cent Bi, 12.5 Cd, 25 Pb, 12.5 Sn; melting point 68°C.; Rose's metal, etc.).   The properties of tin are given in Table III, page 60.   Figure 281 shows the microstructure of a typical

[1] HOYT, "Metallography," vol. II, p. 56, McGraw-Hill Book Company, Inc., New York, 1921.

"National Metals Handbook," American Society for Metals, Cleveland, 1939.

bearing metal of the babbitt type (80 per cent Sn, 15 Sb, 5 Cu). At A is shown a crystal of the antimony-tin compound SbSn, at B the eutectic structure, and at C a crystal, probably of CuSn. If held in the mold a long time, the SbSn crystals will segregate by floating to the top of the mold.[1,2,3]

The lead-tin alloys form the ordinary plumber's solders. The lead-tin diagram is given on page 341.

ZINC AND ITS ALLOYS

Zinc's principal use is as a coating for iron to prevent corrosion as is mentioned on page 317. Such iron is called *galvanized iron.* Its use in brass ranks second. Then follow rolled zinc, die castings, and miscellaneous uses, as in wet batteries, etc. Since cast zinc exhibits long, coarse, columnar crystals and the metal has only one set of slip planes, owing to its hexagonal crystal structure, it is impossible to roll it cold satisfactorily without having first hot-rolled it to break up the columnar structure and induce a recrystallized orientation favorable to further deformation. When cold-worked, zinc recrystallizes at room temperature.

Since iron forms a brittle iron-zinc compound with zinc, its presence above 0.1 per cent is very injurious. This compound is present also under the zinc layer in hot-dipped galvanized iron, as is shown in Fig. 234a, page 318. Cadmium is usually held under 0.005 per cent, lead under 0.007 per cent.

Zinc forms only very limited solutions with other metals, as the diagrams on page 317 show. For die castings, an alloy containing 2.5 to 3.5 per cent copper, 3.5 to 4.5 per cent aluminum, 0.02 to 0.1 per cent magnesium, is used. The decomposition of Al_2Zn_3 at room temperature, which leads to change in dimensions of the casting, does not now seem to cause trouble in this alloy. The Mg is added to counteract a susceptibility to intercrystalline corrosion. The elongation of these alloys at room temperature is practically zero. The zinc-tin alloys contain 80 to 90 per cent zinc, 10 to 20 per cent tin, and usually

[1] HOYT, "Metallography," vol. II, p. 56, McGraw-Hill Book Company, Inc., New York, 1921.

"National Metals Handbook," Amer. Soc. for Metals, Cleveland, 1939.

[2] ELLIS and KARELITZ, *Trans. Am. Soc. Mech. Engrs.,* 1928, MSP 50-11, p. 13.

[3] HUDSON and DARLEY, *J. Inst. Metals,* **24,** 361, 1920.

only 3 to 4 per cent copper.   They are used primarily for bearing metals.

LEAD AND ITS ALLOYS

Lead is useful because of its easy formability, low cost, high specific gravity, low melting point, and good corrosion resistance. It recrystallizes at room temperature after cold work has been performed upon it.   The recrystallization is accelerated by subjecting the lead to vibration.   The lead of the Parkes process contains copper.   In the annealed state it·dissolves rapidly in concentrated sulphuric acid at 160° to 240°C., the attack being principally at the grain boundaries.   Lead from the Pattinson process does not contain copper.   In the annealed state it is insoluble in the above acid up to 300°C.

Lead is frequently alloyed with antimony.   The constitutional diagram and five typical microstructures of these alloys are given on page 159.   There is a slight solubility of antimony in lead at the eutectic temperature (2.45 per cent Sb), decreasing from there down to 0.25 per cent at room temperature.   If quenched in the solid-solution state, these alloys age-harden, enjoying a rise in tensile strength, hardness, and endurance limit.   Quantities of this alloy are used in lead cable sheathing for telephone wires.

Lead alloyed with less than 1 per cent of the alkali metals, as calcium, sodium, lithium, or barium, or with cadmium or arsenic, age-hardens in a similar way.   Such alloys have been used successfully as bearing metals in substitution for the more expensive tin-base bearings.   The lead-antimony alloys have also been used for this purpose.   Lead-tin with Sb and other elements form the most of the solders, while Pb and Sn are important constituents of most of the fusible alloys.

Selected Literature

Trans. Am. Inst. Mining Met. Engrs., **73**, 505, 1926.
Metals & Alloys, **1** (9), 1930.

MAGNESIUM AND ITS ALLOYS

Owing to the ever-increasing modern demand for light metals and alloys for use in the transportation industry, for reciprocating parts, or in any place where it is advantageous to lighten weight, magnesium and its alloys, in both the cast and the worked form,

are rapidly gaining favor. Its lightness (practically two-thirds that of Al), plus its ability to form the basis for high strength alloys, must be balanced against its low resistance to deformation and corrosion for any given service.

Mg, being close-packed hexagonal in structure, has only one slip system on which deformation can take place. The metal work-hardens rapidly and the maximum amount of cold reduction possible is about 6 per cent. However, above 250°C. (the temperature of rapid recrystallization), the metal may be worked with comparative ease. Mg and its alloys may be extruded, rolled, and forged at these elevated temperatures. At room temperature they machine with exceptional ease.

The principal alloying elements for Mg are Al and Zn. The Mg end of both these equilibrium diagrams is eutectic and the alloys are of the precipitation-hardening type. Strengths up to 50,000 lb. per square inch may be obtained in these alloys. Alloys with Cd, Ag, Ca, Ce, and Ni and combinations of these elements with Al, Zn, and Mn are now being investigated, and their future seems promising.

Selected Literature

"National Metals Handbook," American Society for Metals, Cleveland, 1939.

CARPENTER and ROBERTSON: "Metals," Oxford University Press, New York, 1939.

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